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Volumetric Behaviour of the Ethane-Hydrogen Sulfide System

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VOLUMETRIC BEHAVIOUR OF THE ETHANE-HYDROGEN SULFIDE SYSTEM

ABSTRACT

Liquid-vapour equilibrium relations of six mixtures of the ethane-hydrogen sulfide system have previously been studied from the ice point to the cricondentherm for each mixture. The maximum pressure encountered was 1,200 pounds per square inch. It was the purpose of this investigation to extend the volumetric data of this system to higher pressures and to compare the results with other hydrocarbon systems containing hydrogen sulfide.

Six mixtures of different compositions were investigated at $40^{\circ}F$, $100^{\circ}F$ and $160^{\circ}F$ at pressures up to 5,000 pounds per square inch. The volumetric data are tabulated in terms of compressibility factors and also presented in graphical form.

The experimental data were obtained in variable volume apparatus. In this apparatus, the maximum error in the experimental compressibility factor was estimated to be 2.5 percent.

A comparison of the data with a recent correlation and with data for the methane-hydrogen sulfide system for similar concentrations of hydrogen sulfide was made at the same reduced conditions. As expected, the greatest deviation occurs near the two-phase boundary. Here deviations of 20 percent between the experimental points and those predicted by the correlation were not uncommon.

The phase equilibria data of Kay and Brice (6) were used as an aid in defining the compressibility factor curves near the two-phase boundary. The fact that the resulting compressibility factor curves are smooth and consistent is an indication that the present data are reliable.

ACKNOWLEDGEMENTS

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Nomenclature

P   Pressure

R   Universal gas constant

T   Temperature

V   Specific volume

Z   Compressibility factor

Subscripts

C   Critical state

R   Reduced intensive property

1, 2   Pertain to the pure component

X   Mixture of composition $X_1 X_2$

M   Equimolal mixtures

I. INTRODUCTION

The frequent occurrence of hydrogen sulfide in natural gas mixtures from petroleum reservoirs has made desirable more knowledge of the volumetric behaviour of hydrogen sulfide-hydrocarbon systems.

Several extensive investigations of the methane-hydrogen sulfide system have been made (9, 22). Gilliland and Scheeline (5) have made measurements on the hydrogen sulfide-propane system. Their measurements were confined to propane rich mixtures and low pressures. A more complete investigation of saturated mixtures of the propane-hydrogen sulfide system from 32°F to the highest temperature and pressure at which two phases can co-exist was made by Kay and Rambosek (8). Kay and Brice (7) have reported the volumetric relations at the liquid-vapour boundaries of the ethane-hydrogen sulfide system. The highest pressure encountered was the critical pressure of hydrogen sulfide. It was the purpose of this investigation to extend the volumetric data of the ethane-hydrogen sulfide system to higher pressures and to compare the data with a generalized correlation as well as with the data for the methane-hydrogen sulfide system at similar compositions and reduced conditions.

Volumetric data of this type for pure components and gas mixtures have been presented most frequently in the form of generalized compressibility factor charts. The first of these charts was prepared for hydrocarbons by Cope, Lewis and Weber (3) and Brown, Souders and Smith (2). Since then, more extensive efforts have been published. Nelson and Obert (13) have prepared charts based on a

survey of 30 gases as reported in a bibliography of 275 items. Lyderson, Greenkorn and Hougen (10) have investigated the effect of a third parameter, Z_c, (a critical compressibility factor) proposed by Meissner and Seferian (12) as a means of correlation. An extensive set of tables was prepared using volumetric data from 82 compounds. A chart for gas mixtures used considerably in the petroleum industry was prepared by Standing and Katz (25). In preparing these compressibility factor charts, little has been done below a reduced temperature of unity. The most notable exception in this respect is the Pitzer correlation (18) which extends from a reduced temperature of 0.8 to 4.0 and a reduced pressure of 0.2 to 9.0. Since most of the data obtained in the present study was limited to the region of reduced temperature 0.8 to 1.0, Pitzer's correlation was the most suitable for comparison. Macrygeorgos, Robinson and Govier (11) have prepared correction charts, for gas mixtures high in hydrogen sulfide content, to be used in conjunction with the Standing and Katz chart. Accuracy is improved in the regions these correction charts apply, but again the charts are limited to regions of reduced temperature greater than one.

An accurate method of prediction of volumetric data of gas mixtures is needed. The two parameter theory of corresponding states, as first suggested by van der Waals, serves only as a first approximation. A rigorous development of the theory of corresponding states can be obtained if certain assumptions concerning the properties of molecules are made. Pitzer (16, 17), in his development for pure components, made five simplifying assumptions (outlined in the theory section) and concluded that a three parameter function should be used. Subsequently

he extended the correlation to binary gas mixtures (20). Another attempt
at a theoretical treatment for mixtures has been made by Salsburg,
Wojtowicz and Kirkwood (24, 27). The shortcomings of each attempt at
correlation can be attributed to the simplifying assumptions which
must be made to describe very complex molecular behaviour.

II. THEORY

Van der Waals, in 1873 (26), proposed that the behaviour of gases could be described in terms of the deviation of intensive variables from the corresponding critical properties of the system. Although a rigorous development of this theory could not be made originally, knowledge of molecular forces subsequently obtained has permitted this derivation and also suggested improvements to the theory of corresponding states (4, 16, 17, 24).

A development of the theory of corresponding states requires five basic assumptions (17)

1. Classical statistical mechanics can be used for describing molecular motion.

2. The molecules are spherical or freely rotating.

3. The intermolecular vibrations are the same for gas and liquid.

4. The potential energy depends only on the intermolecular distances.

5. The potential curve of a pair of molecules is a universal function.

Although van der Waals empirically proposed a two parameter equation, the theoretical development based on the above assumptions indicated that the volumetric behaviour should be described as a function of three variables. Two critical constants were selected as parameters for each substance. The critical temperature, an obvious choice, characterizes the intermolecular interaction energy. Critical pressure, rather than critical volume was chosen because the former is more easily

determinable and can be obtained with greater accuracy. The third

parameter was chosen as a measure of the deviation of the intermolecular

potential from that of a simple fluid (a fluid whose behaviour conforms

closely to the above assumptions; viz. argon, krypton and xenon). A

convenient empirical quantity is the reduced vapour pressure at a point

well removed from the critical. Because the reduced vapour pressure of

a simple fluid is almost exactly 0.1 at a reduced temperature of 0.7,

it was convenient to take this as a standard. Thus an acentric factor

was defined as

$$\omega = -\log P_R - 1.000$$

with P_R the reduced vapour pressure $(\frac{P}{P_C})$ at $T_R = 0.7$.

Thus the compressibility factor could be expressed as a function of

three variables

$$Z\ (T_R, P_R,\ ) = \frac{PV}{RT} = Z^{\circ} + \ Z'$$

Z° and Z' are each functions of T_R and P_R.

ω, the acentric factor, depends on the substance in question.

Theoretical considerations have shown this acentric factor to depend

on the core radius of a globular molecule, the length of an elongated

molecule or the dipole moment of a slightly polar molecule.

The theory does not hold precisely for pure components, therefore

it can hardly be expected to hold for gas mixtures. The acentric factor

theory has been applied to binary gas mixtures (20) using Kay's rule

to evaluate ω, T_C, and P_C, however in certain systems, better agreement

can be obtained by the introduction of a quadratic term in the

evaluation of the parameters for the mixtures. Hence

$$T_{CX} = X_1 T_{C1} + X_2 T_{C2} + 2X_1 X_2 (2 T_{CM} - T_{C1} - T_{C2})$$

$$P_{CX} = X_1 P_{C1} + X_2 P_{C2} + 2X_1 X_2 (2 P_{CM} - P_{C1} - P_{C2})$$

$$\omega_X = X_1 \omega_1 + X_2 \omega_2 + 2X_1 X_2 (2 \omega_M - \omega_1 - \omega_2)$$

For the twelve systems studied, the quadratic term used in evaluating the pseudo-critical temperature and pressure was found to be significant but the quadratic term in ω was negligible. The deviation from linear dependence does not follow any simple formula based on differences of properties of pure components, thus making prediction difficult. Pitzer does suggest that comparison with systems studied and a consideration of the various factors affecting intermolecular forces should permit reasonable estimates of the quadratic terms.

III.   EXPERIMENTAL EQUIPMENT AND METHOD

The basic parts of the equipment include the high pressure cell, an auxiliary or measuring cell, a positive displacement pump and a pressure measuring device. A schematic diagram of the equipment used in this study is shown in Figure 1.

The main cell, a Ruska PVT cell (Cat. No. 2305), was surrounded by a constant temperature oil bath. The bath temperature was controlled with a relay-delay type circuit using a mercury rotostat sensing device. With this control circuit, no fluctuations of the bath temperature were observed with a standard capillary thermometer. This measuring thermometer which had graduations of approximately six degrees Centigrade per inch allowed the temperature to be measured within ± 0.2 degrees.

Volume measurements in the high pressure cell and pressurizing of the confined gas were achieved with a 250 cc positive displacement Ruska volumetric pump. The pump was calibrated with mercury at room temperature, the required corrections being made for the thermal expansion of the mercury. Data on the density of mercury were obtained from Perry (15). Because the room temperature was relatively constant, thermal expansion of the pump was assumed negligible. The effect of temperature on the volume of the high pressure cell was determined by completely filling the cell with mercury and weighing the overflow for incremental increases of temperature. The volume of the cell increased 0.20 cc for a 60°F rise in temperature.

The increase in volume of the high pressure cell due to pressure was obtained by completely filling the system with mercury and determining
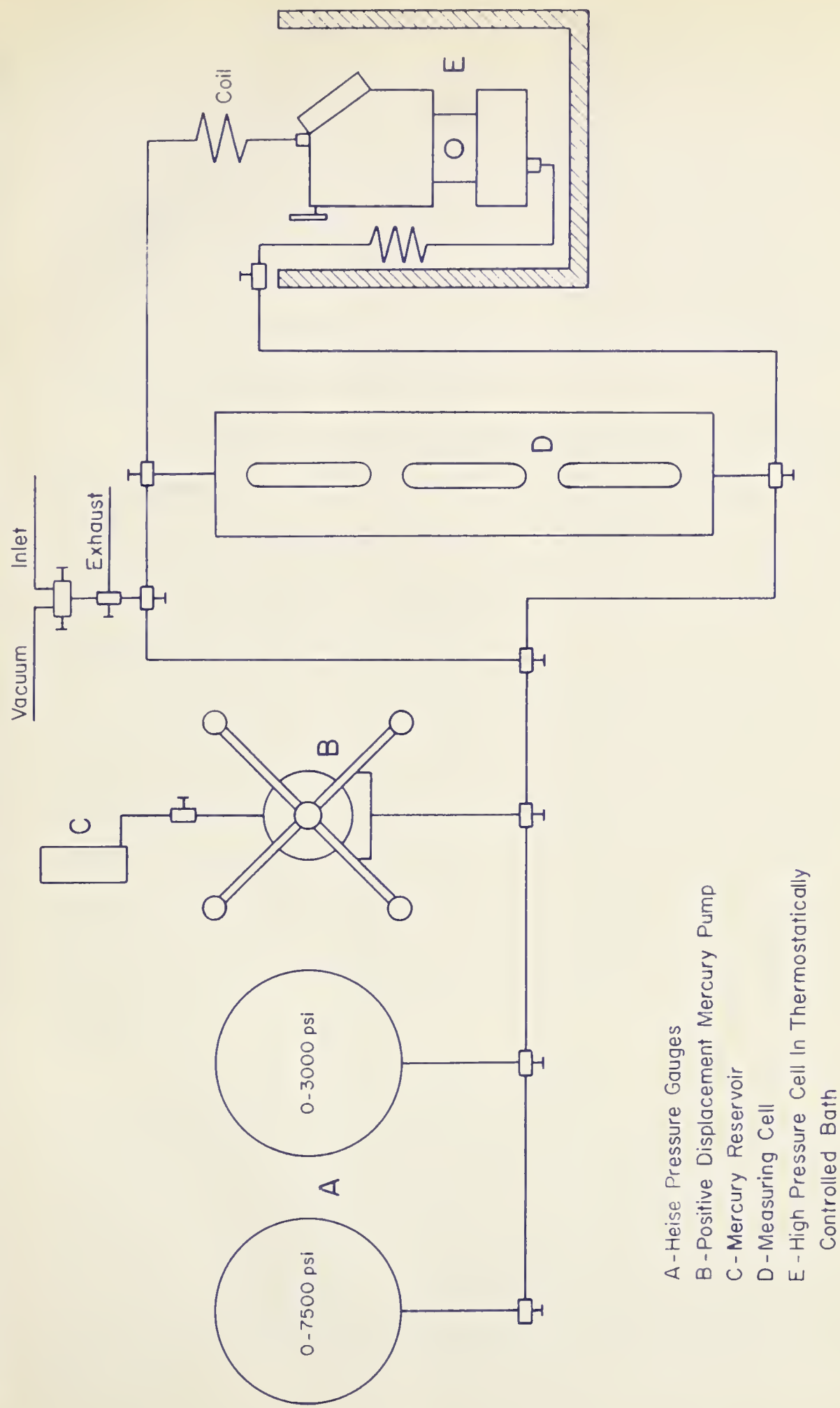
A - Heise Pressure Gauges
B - Positive Displacement Mercury Pump
C - Mercury Reservoir
D - Measuring Cell
E - High Pressure Cell In Thermostatically
    Controlled Bath

FIGURE 1. SCHEMATIC APPARATUS ASSEMBLY.

with the positive displacement pump the volume of mercury required to increase the pressure of the system a definite amount. Eliminating the high pressure cell from the system enabled the determination of the volume increase of the lead lines and pump with pressure. By difference, the increase in volume of the high pressure cell could be calculated. This procedure resulted in a correction of 0.58 cc for every 1,000 pounds per square inch change in pressure. This correction was independent of temperature in the range studied.

A Jerguson liquid level gauge was used as a measuring cell in the preparation of gas mixtures. Mercury was used to calibrate the cell for volume measurements. The mercury level in the cell was determined with a 100 cm Gaertner cathetometer and was referenced to a datum point marked on the body of the cell.

Pressure measurements were made with calibrated sixteen inch Heise bourdon type gauges. Measurements were within $\pm$ 2 and $\pm$ 5 pounds per square inch on the 3,000 and the 7,500 pounds per square inch gauges respectively. The gauges were on the mercury side of the circuit and hydrostatic head corrections were applied. The cathetometer was used to determine the hydrostatic head component of the measured pressures.

In the tests made, it was necessary to charge the high pressure cell with a known amount of each gas. For this, the equipment which consisted of the high pressure cell, the auxiliary cell and necessary lead lines, was first evacuated to a pressure of 0.1 mm of mercury with a duoseal vacuum pump. Clean mercury was then allowed to flow into this evacuated space, thereby minimizing the amount of air trapped in the system.

The gases charged to the high pressure cell were first passed over activated alumina and coconut charcoal. The effect of this simple purification on ethane was not determined, but very significant reduction in the rate of reaction between hydrogen sulfide and mercury was observed. Although some reaction was still observed, it is not believed that the results obtained have been significantly affected. This has been confirmed to some extent by the agreement of experimental and published data. (Figure 2)

The least volatile component was introduced first into the high pressure cell by removing a definite volume of mercury with the positive displacement pump. The number of moles of gas in the high pressure cell were determined at low pressures using compressibility factor charts available in the literature for the pure components. The second gas was introduced into the auxiliary cell, the volume being determined with the cathetometer and the calibration curves. The connecting line between the auxiliary cell and the high pressure cell was filled with mercury. Then the transfer of gas was made by positive displacement with mercury. Knowing the original volume of the second gas in the auxiliary cell, and the amount of mercury used in transfer, the volume charged to the high pressure cell could readily be determined.

The mixture was now confined within the steel pressure vessel. Thorough mixing was attained by vigorous agitation. This was continued until a constant pressure reading was obtained. The constant pressure reading was the criterion of an equilibrium state.

The volume of the chamber available to the gas mixture was changed by introducing or withdrawing mercury in known quantities.

Using the calibrations previously obtained, the necessary corrections to the volume of the gas were made. The pressure and compressibility factors were determined for a series of states for each of a number of systematically chosen temperatures.

A check on the calibration of the equipment was made using the pure components, ethane (1, 23), hydrogen sulfide (21) and methane (14), and comparing the observed compressibility factors with published values. As a further indication of adequacy of the procedures and equipment used, tests were made on the known system, methane-hydrogen sulfide for which compressibility factors are available in the literature (22). The results of these tests, along with the literature values, are shown in Figure 2.

The hydrogen sulfide used was supplied by the Matheson Co. and the ethane by Phillips Petroleum Co. Both had a stated minimum purity of 99 mole percent.

The mercury was periodically drained from the system and cleaned in a mercury oxifier made by the Bethlehem Apparatus Co. A mercury filter, type F (Gold Adhesion principle), supplied by the same company was used to filter the oxified mercury.
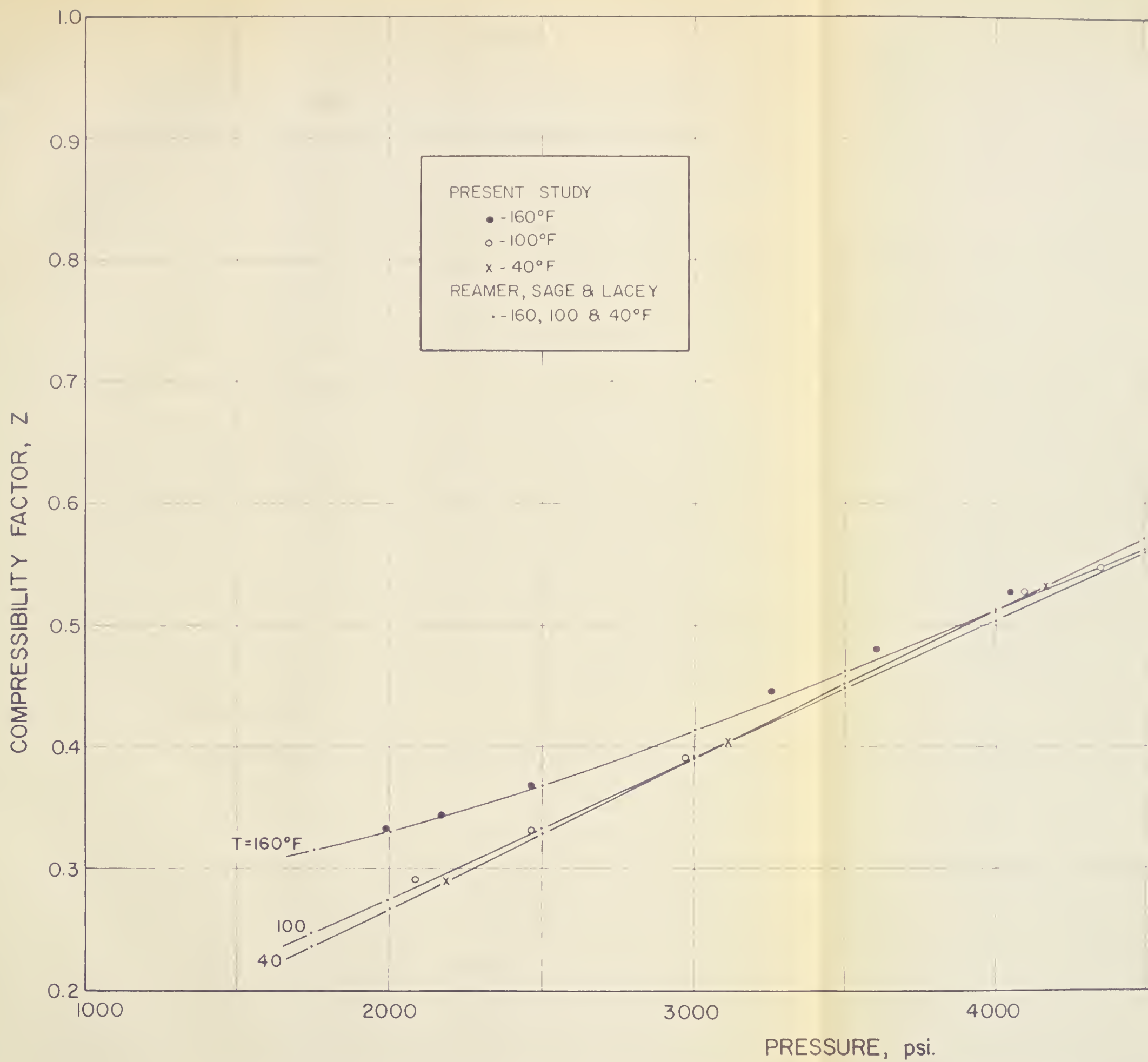
FIGURE 2. COMPARISON BETWEEN EXPERIMENTAL AND PUBLISHED COMPRESSIBILITY FACTO
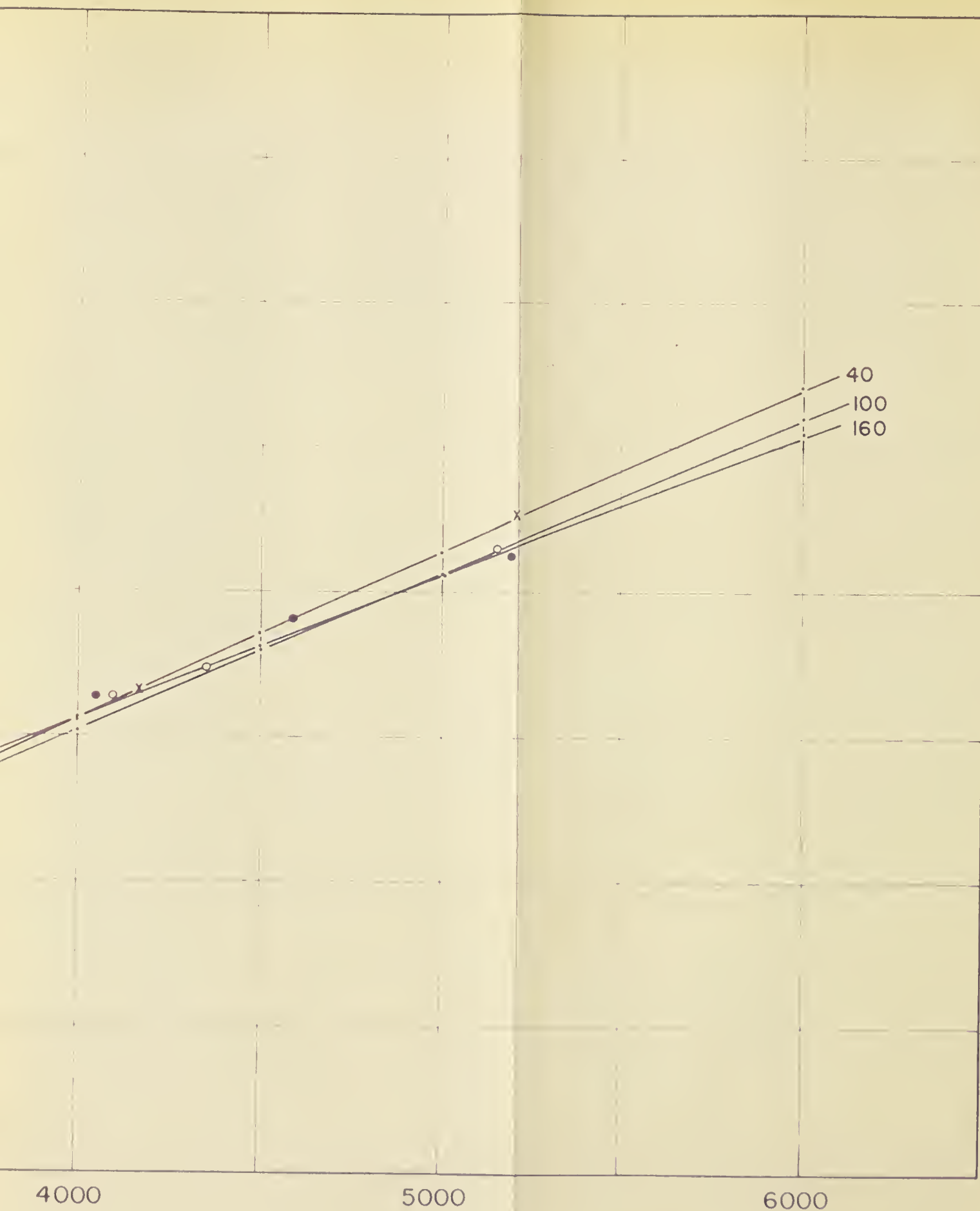
COMPRESSIBILITY FACTORS FOR THE SYSTEM METHANE-HYDROGEN SULFIDE.

IV. EXPERIMENTAL RESULTS

Volumetric data were obtained for six mixtures of ethane and hydrogen sulfide at temperatures of 40°F, 100°F and 160°F, and at pressures to 5,000 pounds per square inch. The compressibility factors obtained from these data are tabulated in Table 1. The probable uncertainty in compressibility factors for pressures less than 3,000 pounds per square inch has been estimated at 1.9 percent, while for higher pressures, the uncertainty may be as high as 2.5 percent, (see calculation of errors in Appendix).

In addition to tabulated values, the data have been presented graphically, (Figures 3 to 8). The compressibility factors are shown as a function of the pseudo-reduced pressure for constant pseudo-reduced temperature. In each of these figures, the relation is given for three pseudo-reduced temperatures (corresponding to the three experimental temperatures, 40°F, 100°F and 160°F) at a given composition. The pseudo-reduced temperature and pressure were calculated according to the methods proposed by Kay (6).

The two phase boundaries were established from the phase data of Kay and Brice (7). In order to obtain compressibility factors for the same conditions of temperature, pressure, and composition as the present investigation, interpolation with respect to these variables was required. The results obtained by interpolation on large scale crossplots have been shown in several figures, and in each case the source is designated on the figure. The agreement between the compressibility factor curves obtained in this investigation
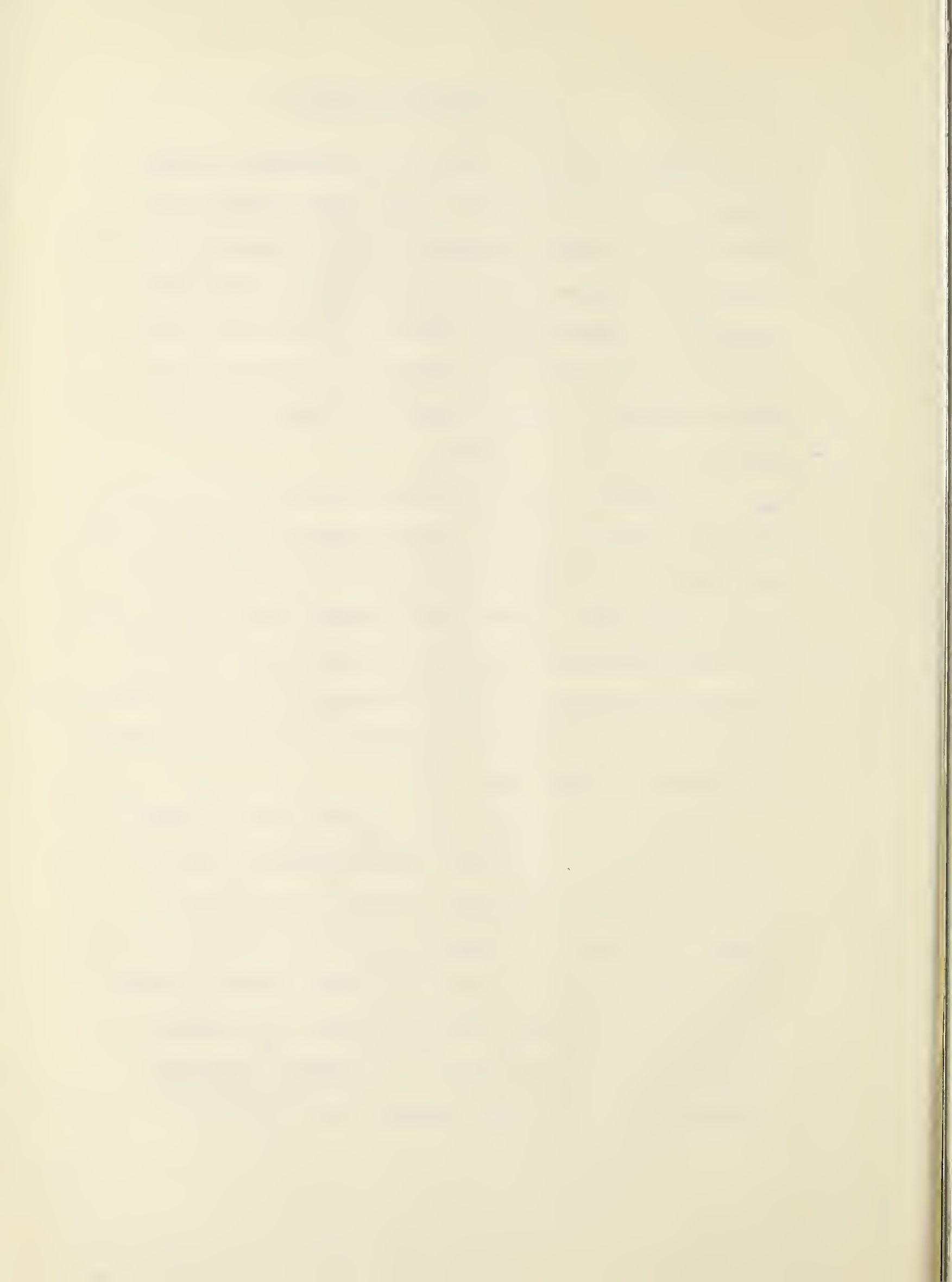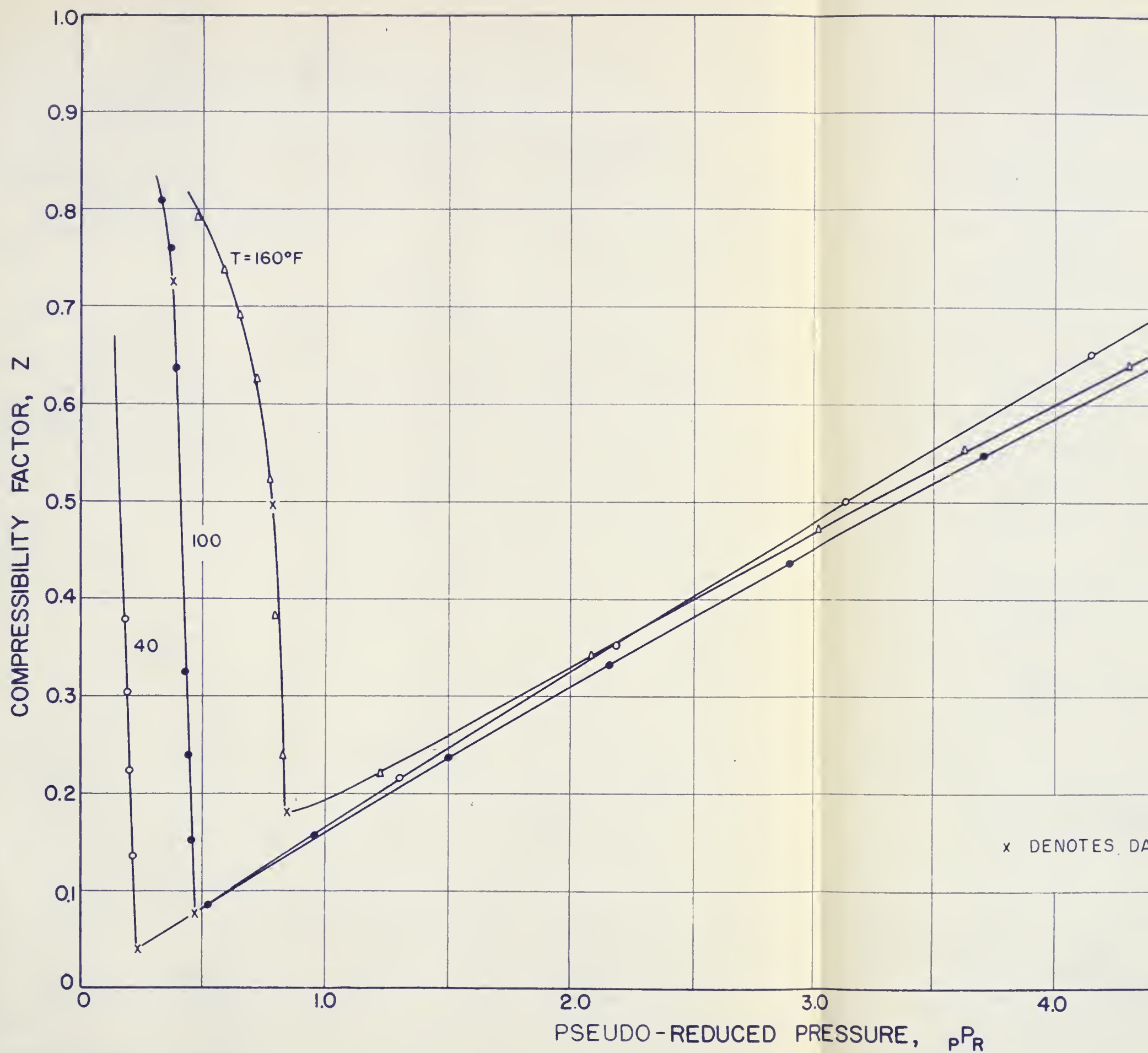
FIGURE 3. COMPRESSIBILITY OF A MIXTURE CONTAINING 0.157 MOLE FRACTION
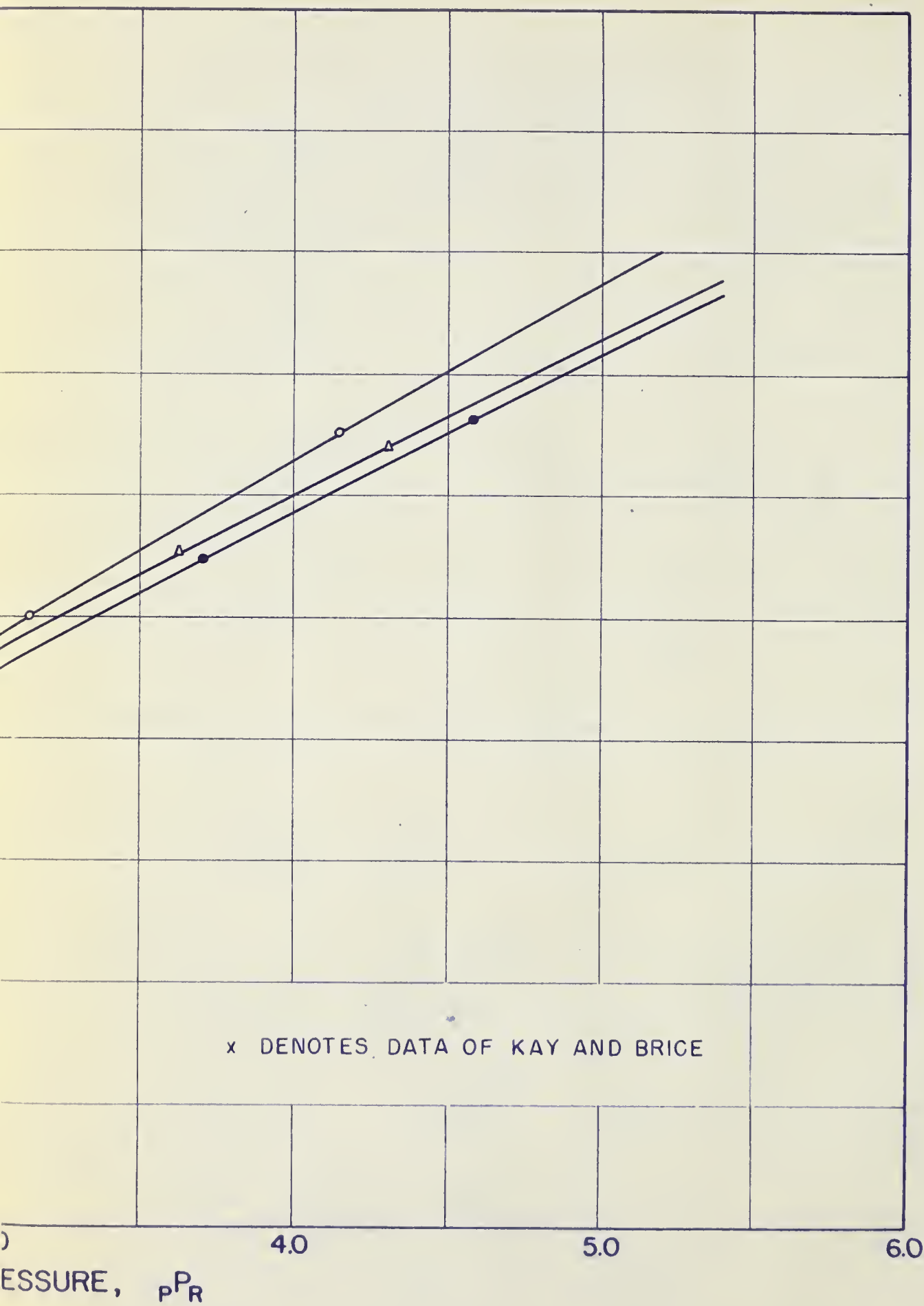
x DENOTES DATA OF KAY AND BRICE

ESSURE, $_pP_R$

ONTAINING 0.157 MOLE FRACTION ETHANE.
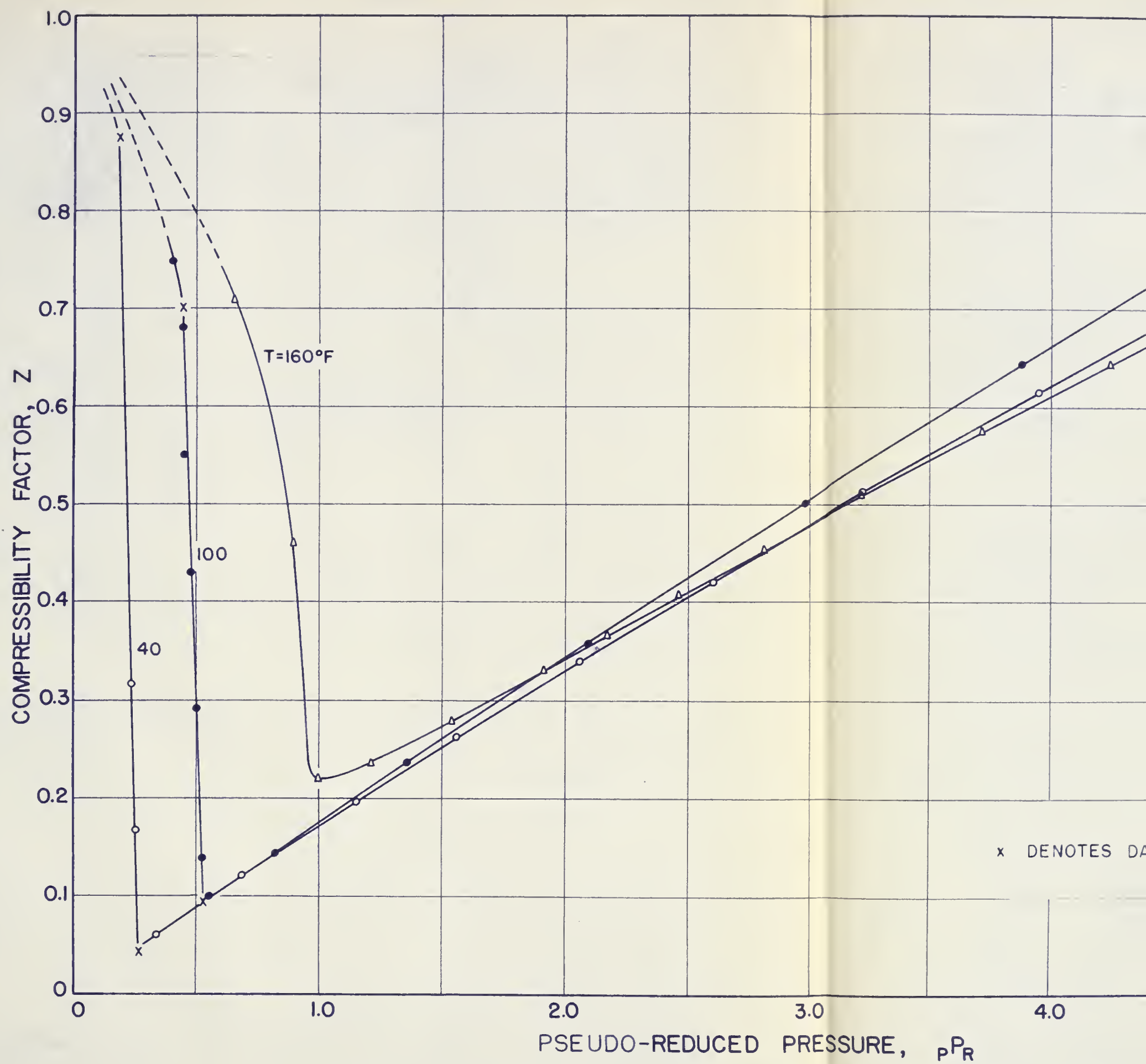
FIGURE 4. COMPRESSIBILITY OF A MIXTURE CONTAINING 0.242 MOLE FRACT

x   DENOTES DATA OF KAY AND BRICE

4.0   5.0   6.0

SSURE, $_PP_R$

NTAINING 0.242 MOLE FRACTION ETHANE.
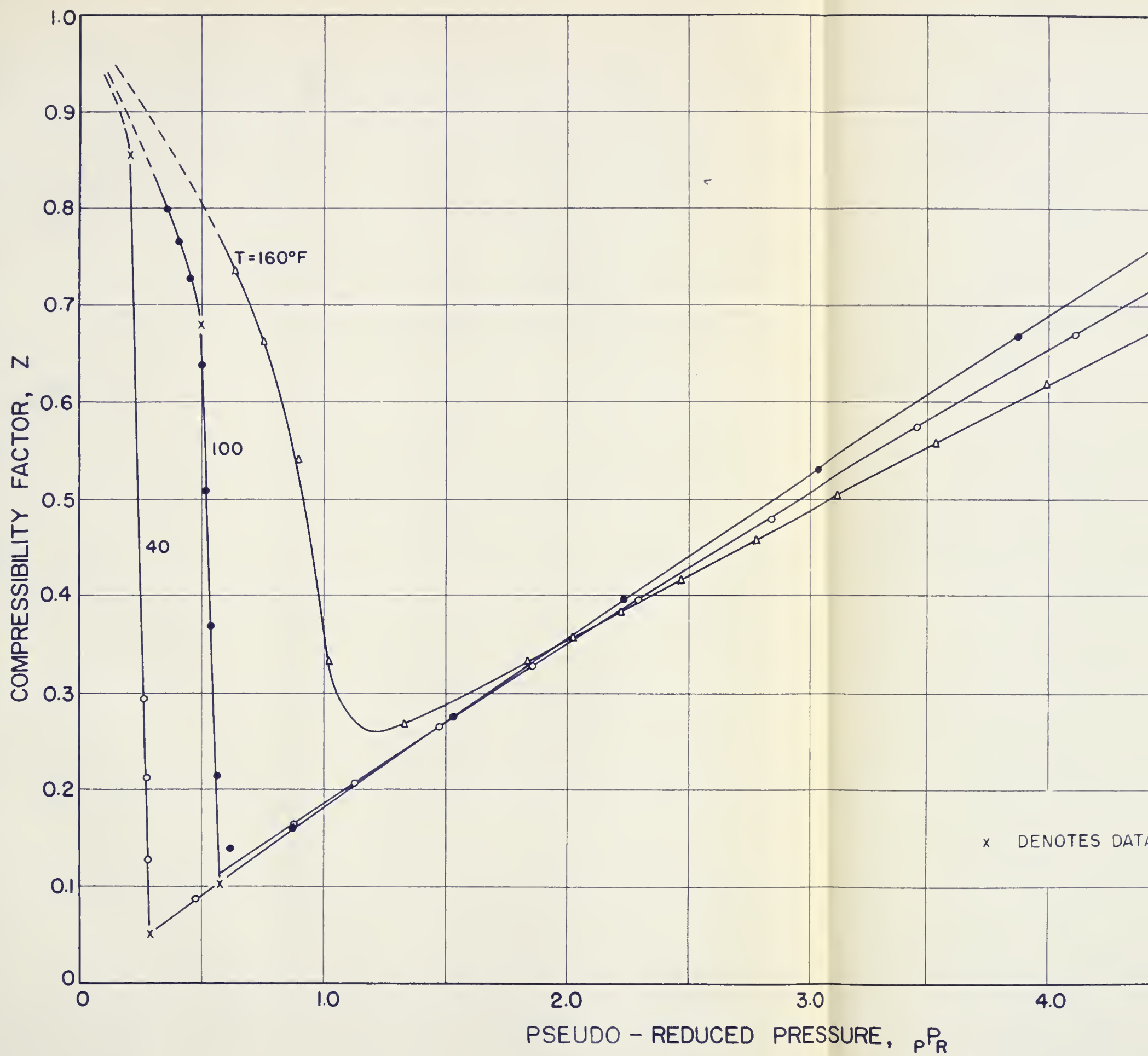
FIGURE 5. COMPRESSIBILITY OF A MIXTURE CONTAINING 0.299 MOLE FRACT

SURE, $_pP_R$
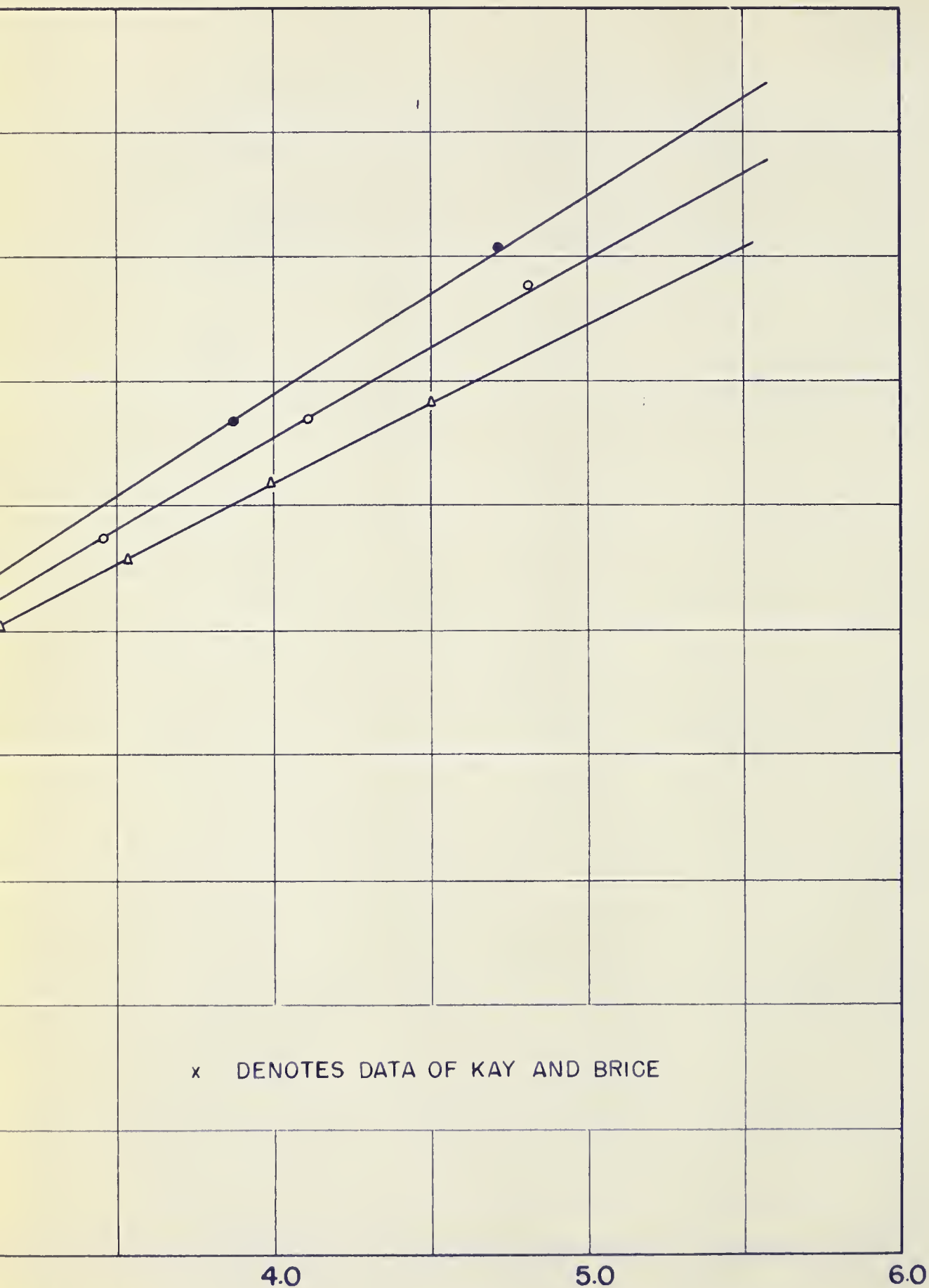
NTAINING 0.299 MOLE FRACTION ETHANE.
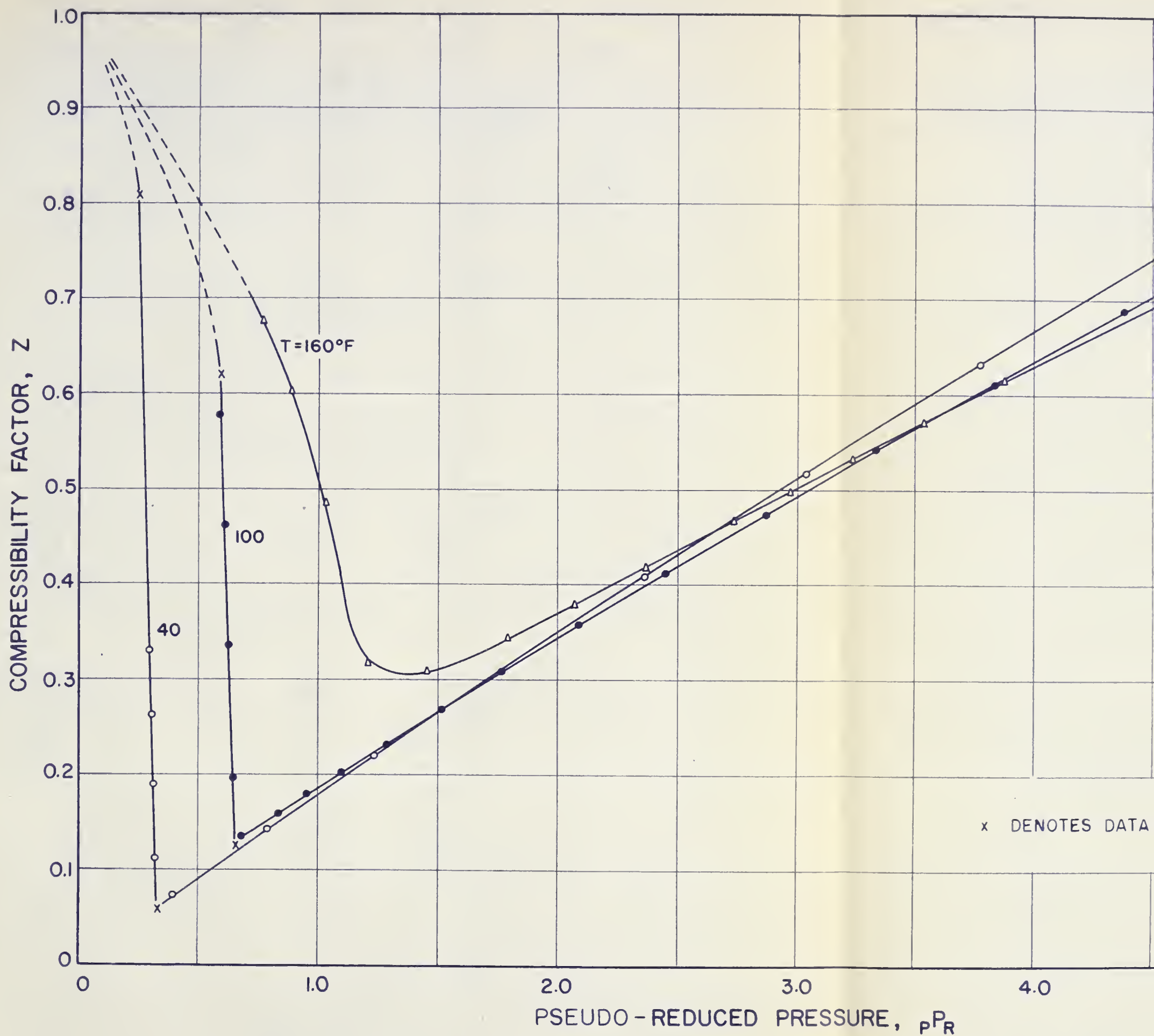
FIGURE 6. COMPRESSIBILITY OF A MIXTURE CONTAINING 0.409 MOLE FRACTION
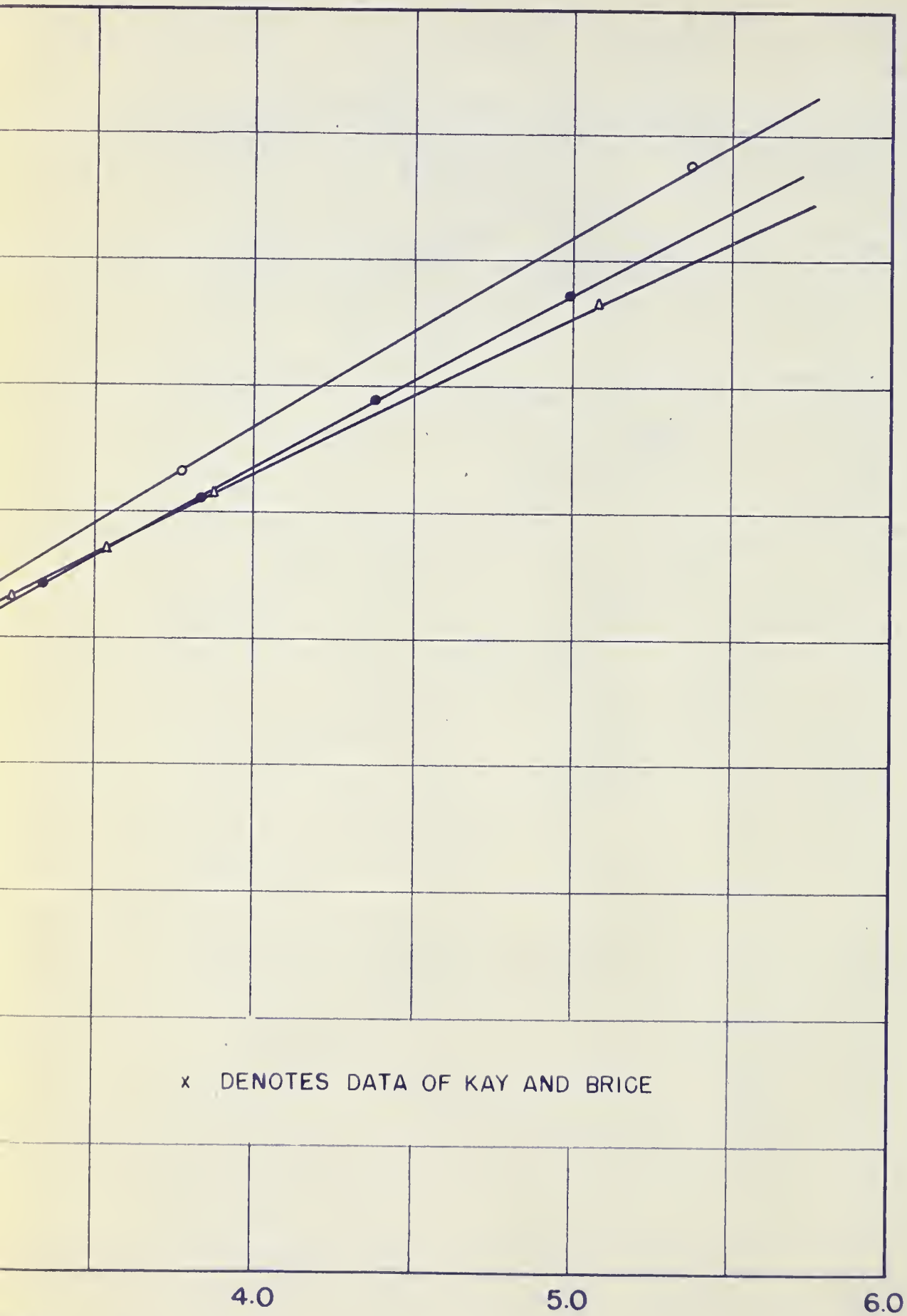
PRESSURE, $_PP_R$

...AINING 0.409 MOLE FRACTION ETHANE.
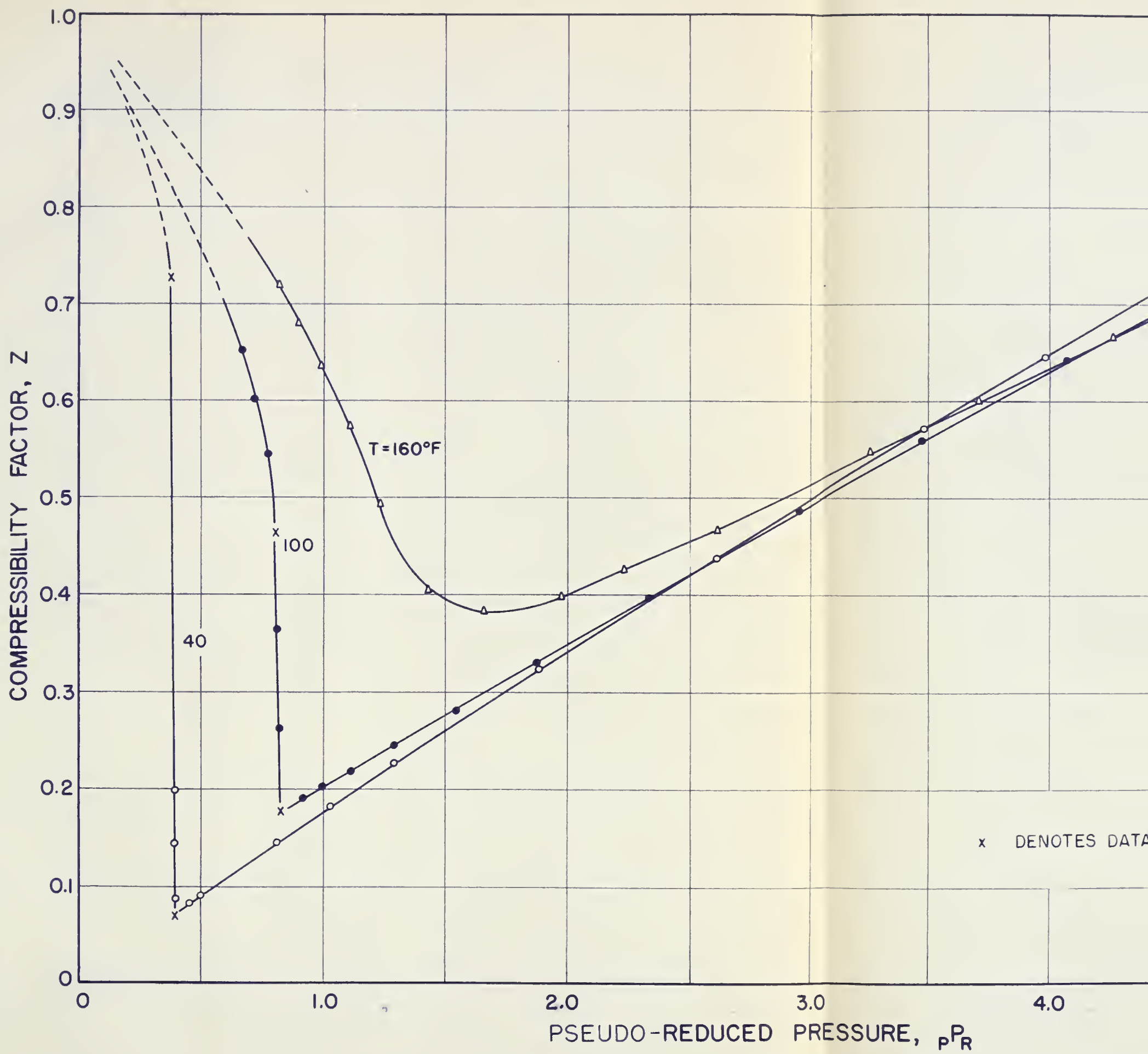
FIGURE 7. COMPRESSIBILITY OF A MIXTURE CONTAINING 0.618 MOLE FRACT

4.0   5.0   6.0

x   DENOTES DATA OF KAY AND BRICE
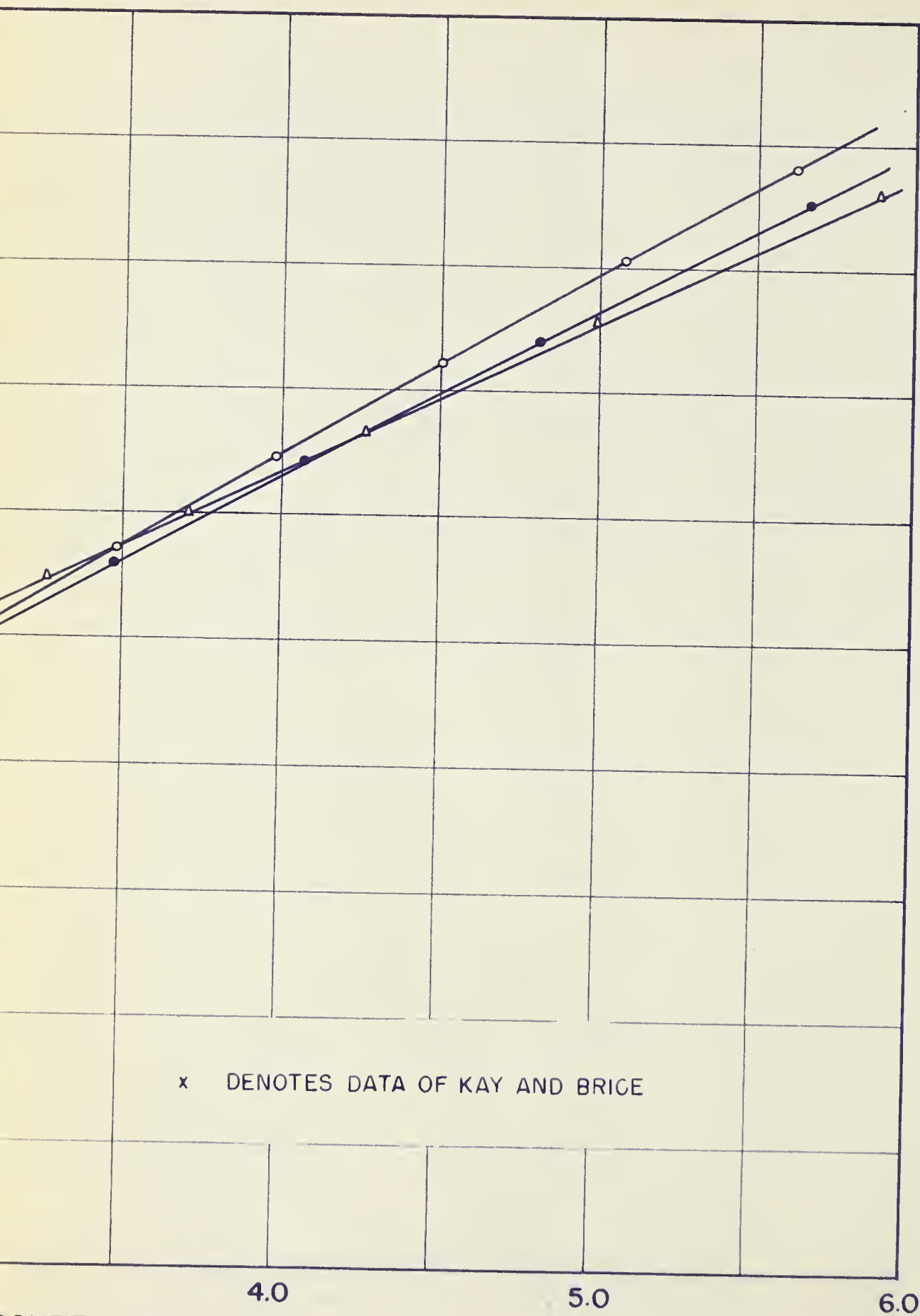
SSURE, $_PP_R$

NTAINING 0.618 MOLE FRACTION ETHANE.
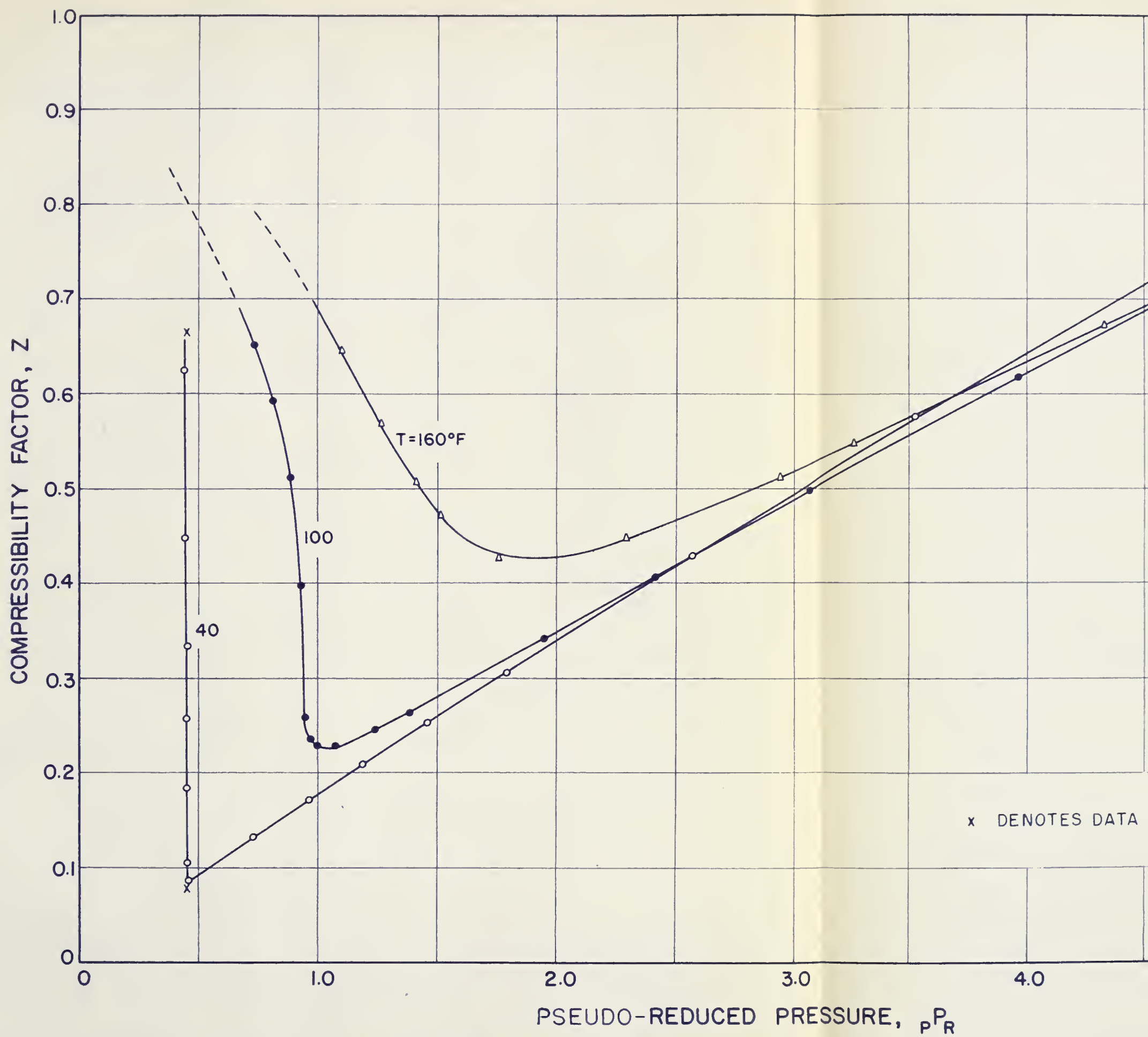
FIGURE 8. COMPRESSIBILITY OF A MIXTURE CONTAINING 0.773 MOLE FRACTION

SSURE, $_pP_R$
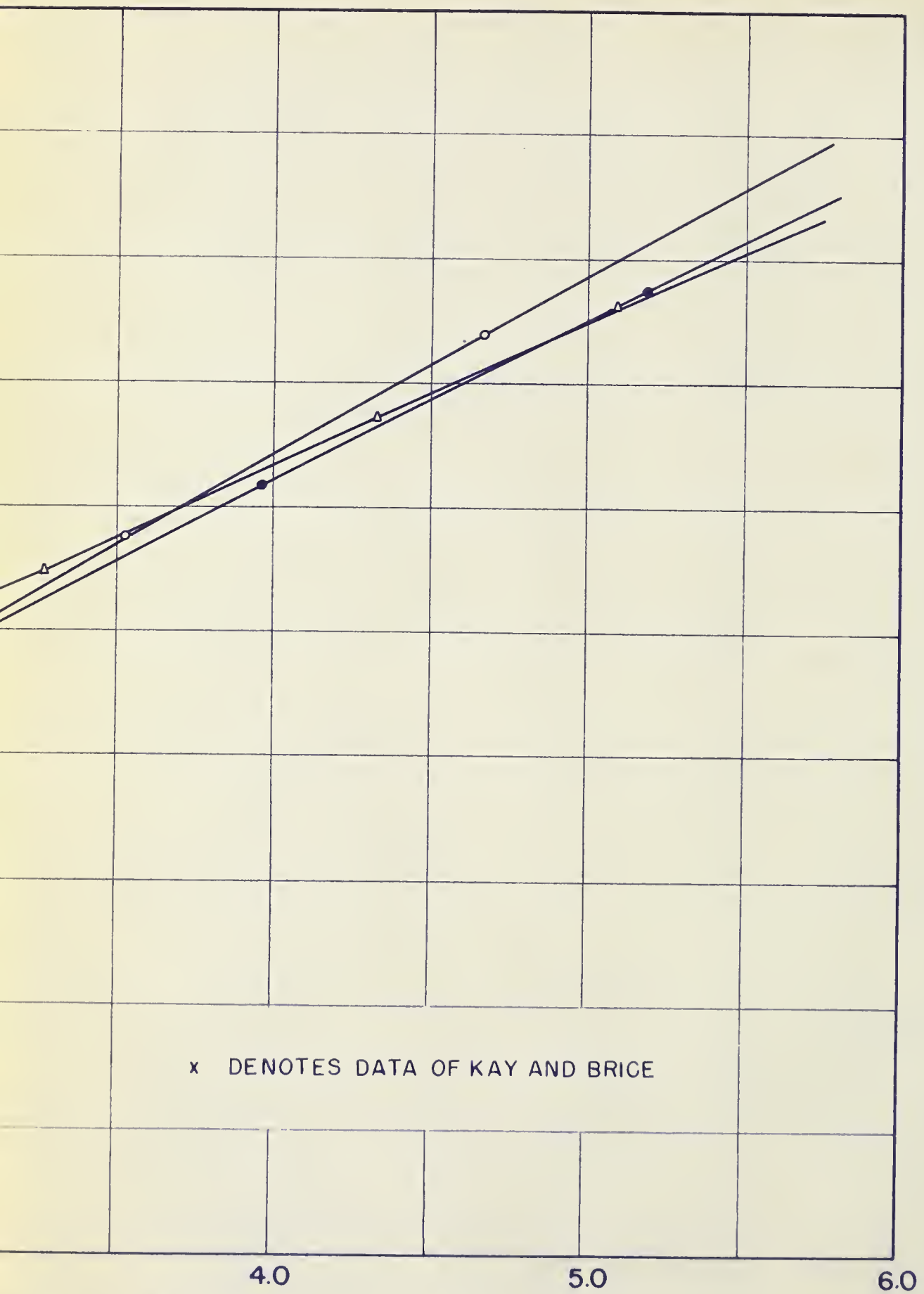
NTAINING 0.773 MOLE FRACTION ETHANE.

x   DENOTES DATA OF KAY AND BRICE

(Figures 3 to 8) and the values interpolated from the data of Kay and Brice (7) served as a check on the accuracy of the present results.

Plots of compressibility values against composition under isobaric-isothermal conditions supplied a further check on the consistency of the results. These curves were found to extrapolate well to the limiting values representing the volumetric behaviour of pure components. Figures 9, 10 and 11 illustrate the type of relation obtained for the three temperatures investigated. The discontinuity in the curve for a pseudo-reduced temperature equal to unity, in Figure 9, is characteristic of a phase transition, while in the single phase region, the expected smooth curve between the values for the two pure components was obtained. Similar comments can be made about the curves in Figures 10 and 11.

The compressibility factor curves obtained in this investigation and shown in Figures 5 to 10, are qualitatively similar to those presented in the literature for other systems. For decreasing pressure, below the dew point, the compressibility factor tends to unity. While at pressures greater than the bubble point pressure, the compressibility factor tends to increase. The compressibility factor varies linearly with the pseudo-reduced pressure in the two phase region. At temperatures greater than the critical temperature, a continuous curve having the expected form is obtained.
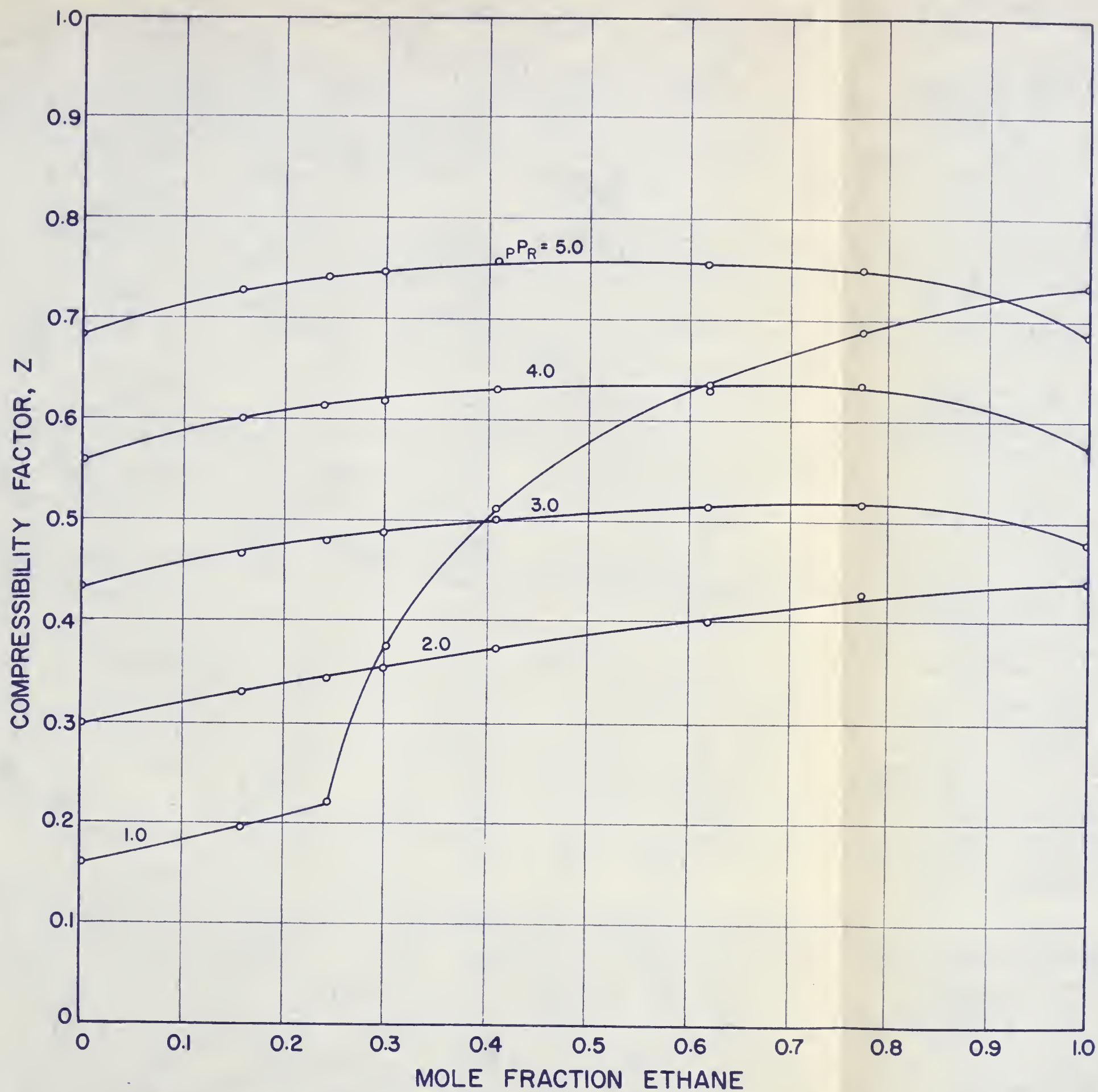
FIGURE 9. ISOBARIC EFFECT OF COMPOSITION ON COMPRESSIBILITY FACTOR AT 160°F.

0.8   0.9   1.0
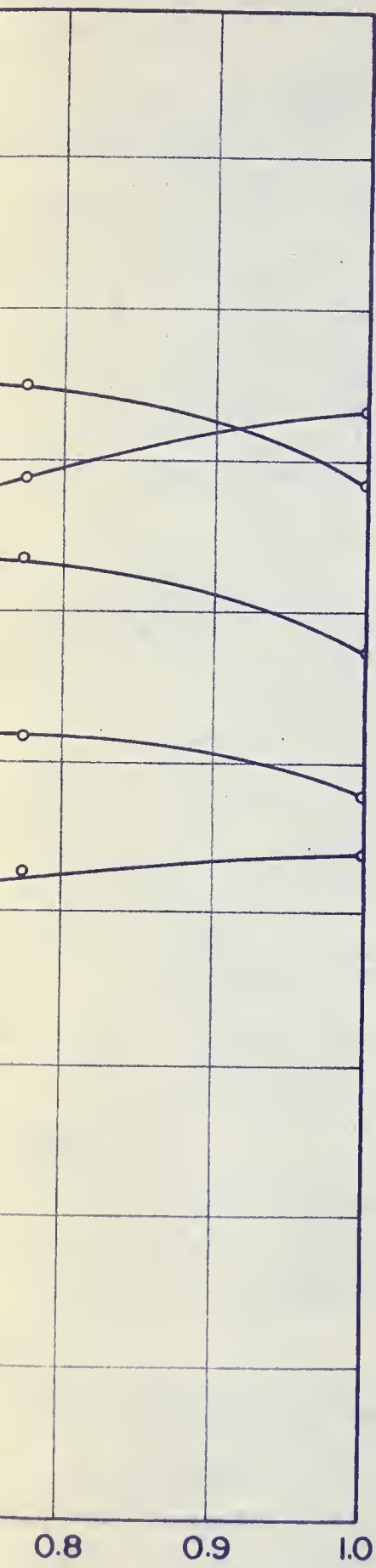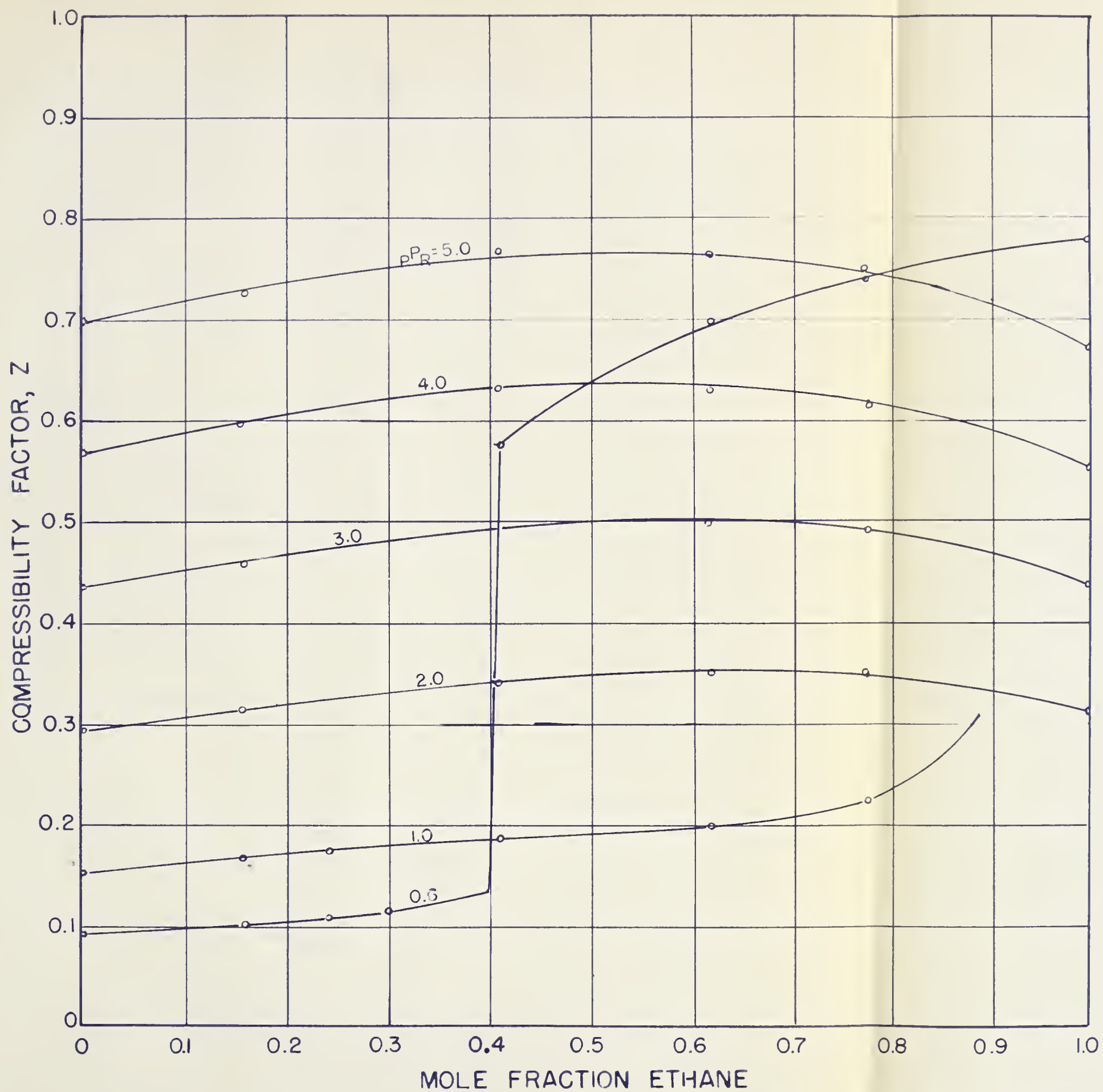
Y FACTOR AT 160°F.

FIGURE 10. ISOBARIC EFFECT OF COMPOSITION ON COMPRESSIBILITY FACTOR AT 100°F.

0.8   0.9   1.0
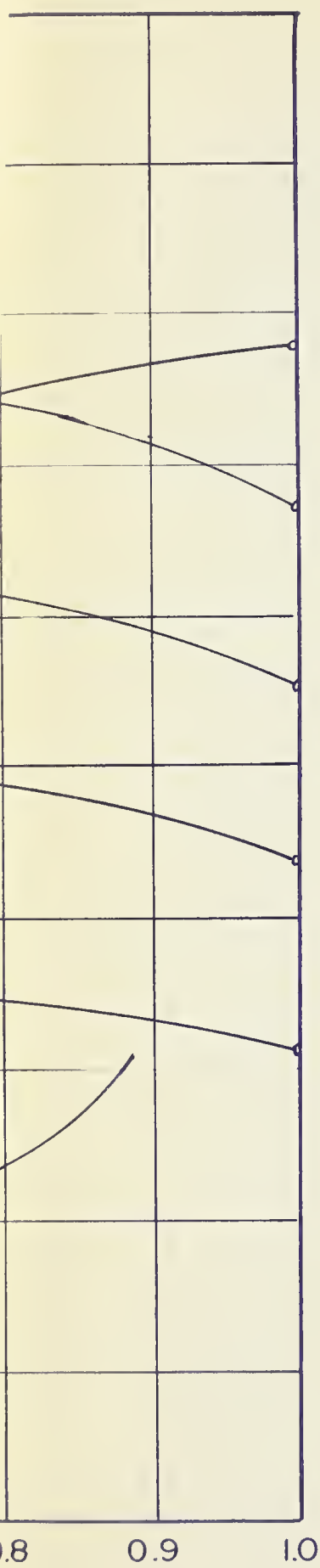
FACTOR AT 100°F.
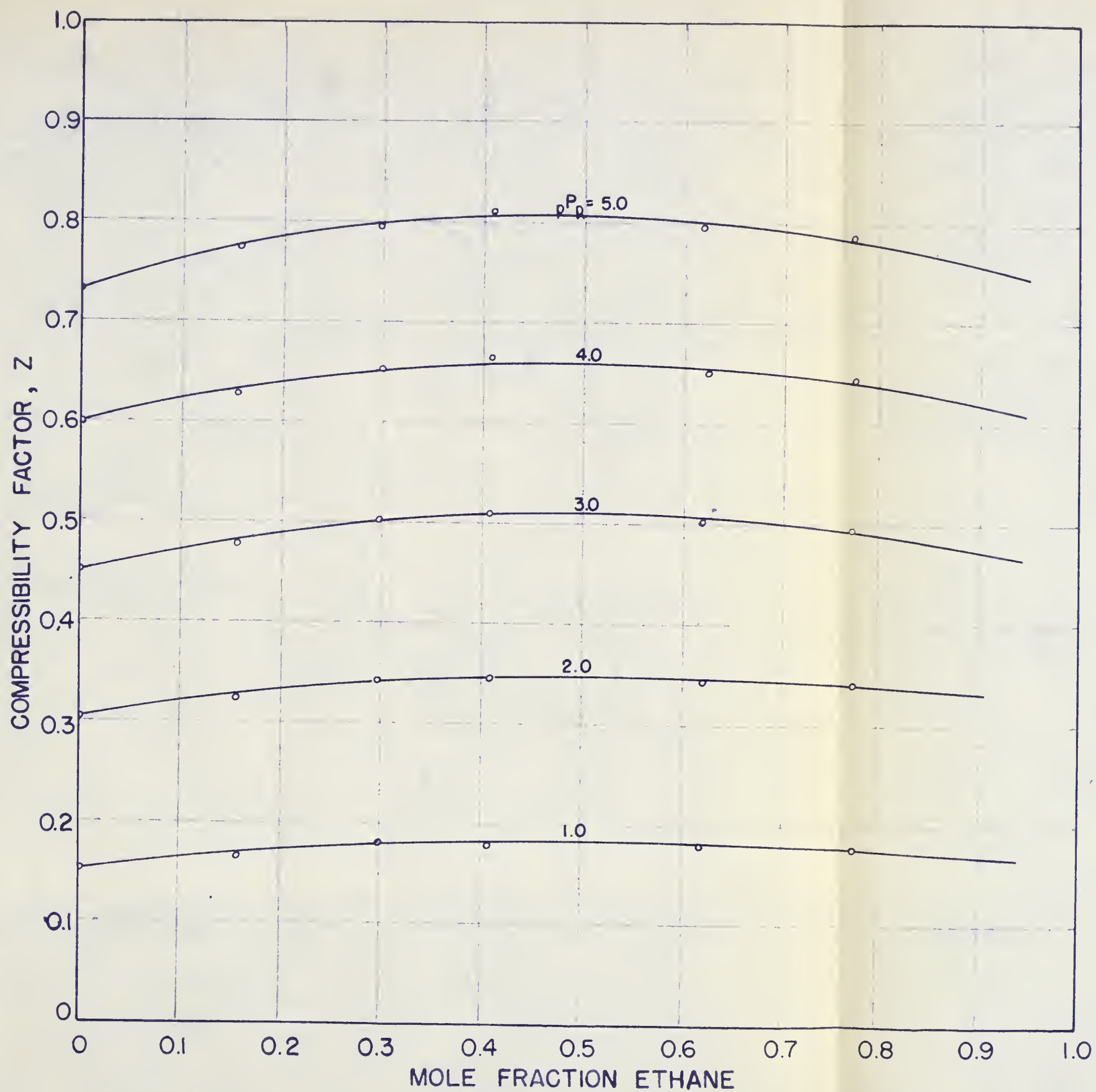
FIGURE 11. ISOBARIC EFFECT OF COMPOSITION ON COMPRESSIBILITY FACTOR AT 40°F.

0.8   0.9   1.0
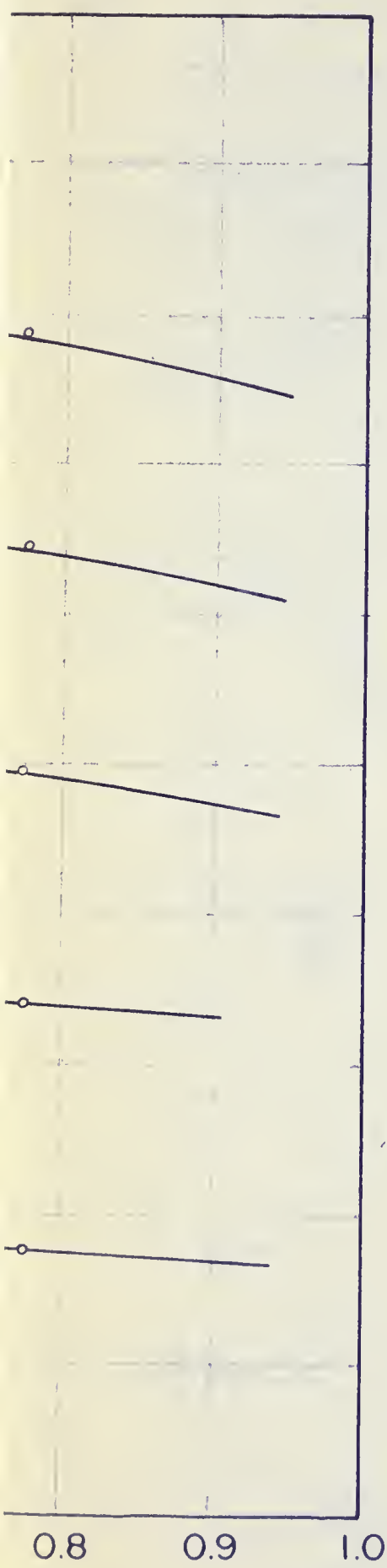
TY FACTOR AT   40°F.

V. CONCLUSIONS AND RECOMMENDATIONS

The experimental compressibility factors obtained are within the limits of uncertainty stated previously. This is indicated by the checks with literature values of phase behaviour and volumetric data, (Figures 3 to 11 inclusive).

A comparison between the experimental data and Pitzer's correlation is shown in Figure 12 for the systems ethane-hydrogen sulfide and methane-hydrogen sulfide. Kay's rule was used in evaluating the compressibility factors using Pitzer's correlation. Table 2 contains the points of this investigation for which a comparison could be made with either Pitzer's correlation, the data for the methane-hydrogen sulfide system or both.

Comparison of the data for the system ethane-hydrogen sulfide with Pitzer's correlation indicated deviations as great as 40 percent. The values of compressibility factor obtained from the correlation were at all times lower than the experimental values. A similar behaviour was obtained for the system methane-hydrogen sulfide, although the greatest error encountered here was only 30 percent. The discrepancies for both systems were rather large. The area of greatest deviation is, as expected, near the two phase region.

This discrepancy may be due to inadequate means of predicting pseudo-critical properties. These were predicted with the linear relationships in composition proposed by Kay (6). However, it has been suggested (20) that the pseudo-critical behaviour could be better described with a quadratic equation. The difficulty, however, is the unavailability of data to predict the quadratic terms. The quadratic
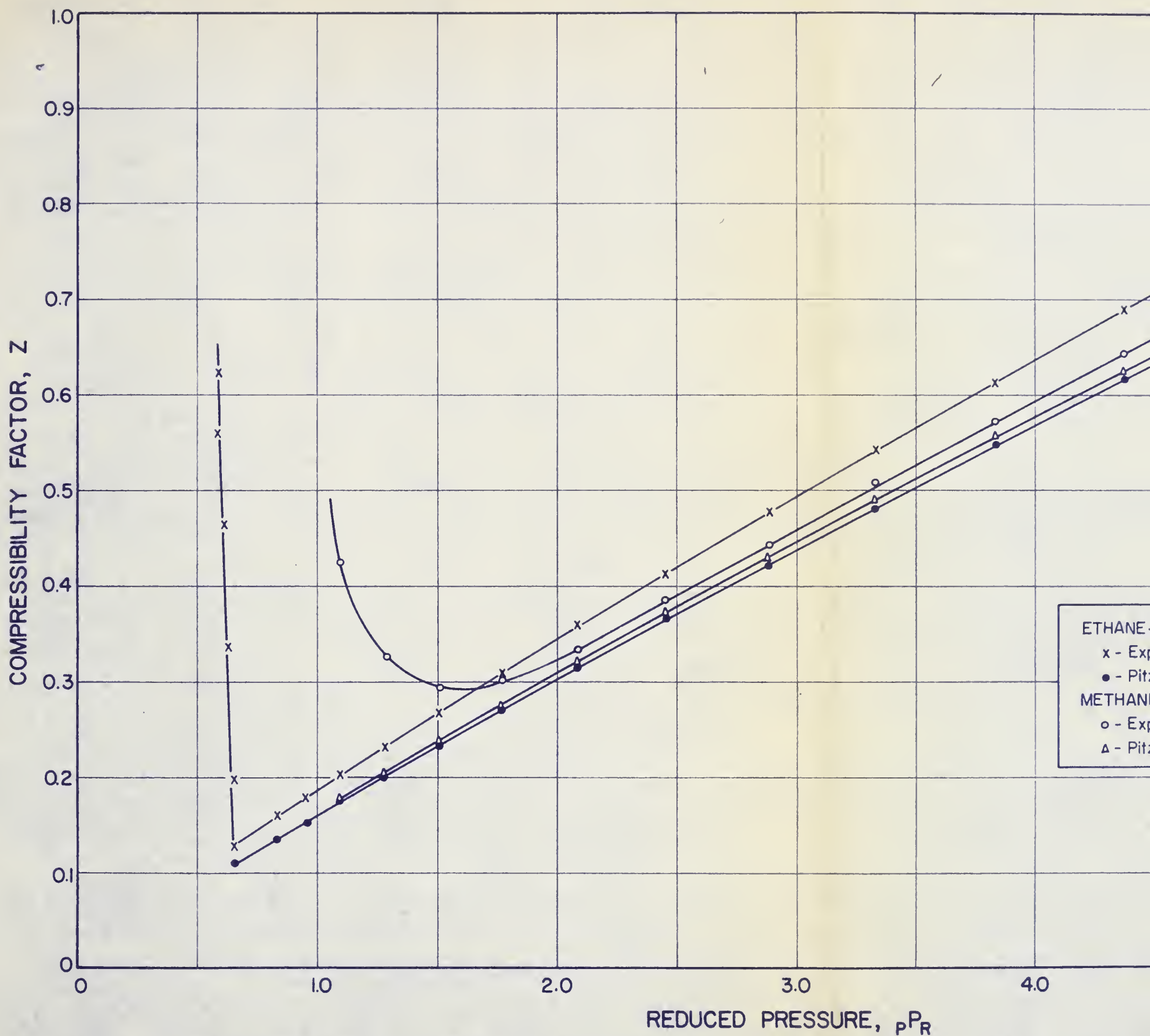
FIGURE 12. PREDICTED AND EXPERIMENTAL COMPRESSIBILITY FACTORS FOR THE SYSTEMS ETHANE-H
METHANE-HYDROGEN SULFIDE. Data evaluated for 0.409 mole fraction hydrogen sulfide at $_pT$
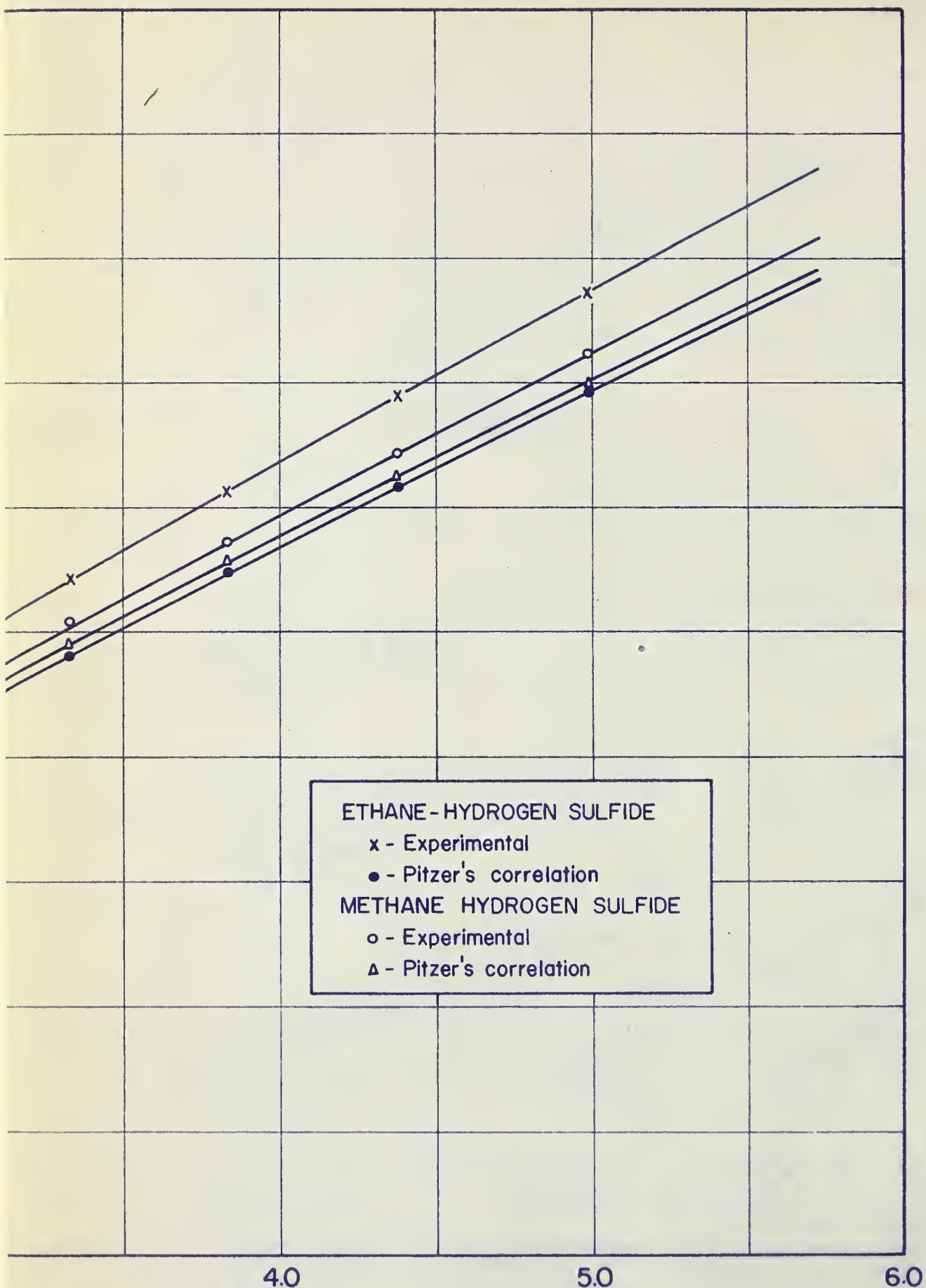
FOR THE SYSTEMS ETHANE-HYDROGEN SULFIDE AND
le fraction hydrogen sulfide at $_PT_R = 0.900$.

ETHANE-HYDROGEN SULFIDE
x - Experimental
● - Pitzer's correlation
METHANE HYDROGEN SULFIDE
o - Experimental
△ - Pitzer's correlation

terms obtained from previous studies showed no means of correlation.
Nevertheless, prediction is possible on the basis of statistical
mechanical properties of the molecules involved.

Pitzer's correlation for predicting the volumetric properties,
though very satisfactory for pure components, has its limitations when
extended to binary or more complex gas mixtures. Further research
could render this three parameter correlation applicable equally well
to gas mixtures as well as to pure components.

BIBLIOGRAPHY

1. Barkelew, C.H., Valentine, J.L., and Hurd, C.O.,
    Trans. Am. Inst. Chem. Eng., $\underline{43}$, 25 (1947).

2. Brown, G.G., Souders, M., and Smith, R.L.,
    Ind. and Eng. Chem., $\underline{24}$, 513 (1932).

3. Cope, J.Q., Lewis, W.K., and Weber, H.C.,
    Ibid., $\underline{23}$, 887 (1931).

4. de Boer, J., and Michels, A.,
    Physica, $\underline{5}$, 945 (1938).

5. Gilliland, E.R., and Scheeline, H.W.,
    Ind. and Eng. Chem., $\underline{32}$, 48 (1940).

6. Kay, W.B., Ibid., $\underline{28}$, 1014 (1936).

7. Kay, W.B., and Brice, D.B., Ibid., $\underline{45}$, 615 (1953).

8. Kay, W.B., and Rambosek, G.M., Ibid., $\underline{45}$, 221 (1953).

9. Kohn, J.P., and Kurata, F., A.I.Ch.E., $\underline{4}$, 211 (1958).

10. Lyderson, A.L., Greenkorn, R.A., and Hougen, O.A.,
    Generalized Thermodynamic Properties of Pure Fluids,
    Univ. Wisc. Eng. Expt. Sta. Rept. 4, (1955).

11. Robinson, D.B., Macrygeorgos, C.A., and Govier, G.W.,
    J. Pet. Tech., $\underline{219}$, 37A (1960).

12. Meissner, H.P., and Seferian, R.,
    Chem. Eng. Prog., $\underline{47}$, 579 (1954).

13. Nelson, L.C., and Obert, E.F., Mech. Eng., $\underline{76}$, 280 (1954).

14. Olds, R.H., Reamer, H.H., Sage, B.H., Lacey, W.N.,
    Ind. and Eng. Chem., $\underline{35}$, 922 (1943).

15. Perry, J.H., Chemical Engineer's Handbook,
    McGraw-Hill Book Co., Inc., New York (1950).

16. Pitzer, K.S., J. Chem. Phys., $\underline{7}$, 583 (1939).

17. Pitzer, K.S., J. Amer. Chem. Soc., $\underline{77}$, 3427 (1955).

18. Pitzer, K.S., Lippmann, D.Z., Curl Jr., R.F.,
    Higgins, C.M., Petersen, D.E., Ibid., $\underline{77}$, 3433 (1955).

19.   Pitzer, K.S., and Curl Jr., R.F., Ibid., 79, 2369 (1957).

20.   Pitzer, K.S., and Hultgren, G.C., Ibid., 80, 4793 (1958).

21.   Reamer, H.H., Sage, B.H., and Lacey, W.N.,
       Ind. and Eng. Chem., 42, 140 (1950).

22.   Reamer, H.H., Sage, B.H., and Lacey, W.N.,
       Ind. and Eng. Chem., 43, 976 (1951).

23.   Sage, B.H., Webster, D.C., and Lacey, W.N.,
       Ibid., 29, 662 (1937).

24.   Salsburg, Z.W., Wojtowicz, P.J., and Kirkwood, J.G.,
       J. Chem. Phys., 26, 1533 (1957).

25.   Standing, M.B., and Katz, D.L.,
       Trans. A.I.M.E., 146, 140 (1942).

26.   van der Waals, J.H., Dissertation, Leiden (1873).

27.   Wojtowicz, P.J., Salsburg, Z.W., and Kirkwood, J.G.,
       J. Chem. Phys., 27, 505 (1957).

APPENDIX

ESTIMATE OF ERROR

The values of the three variables, (pressure, temperature and volume) are required to calculate the compressibility factor of a known quantity of gas. These variables were measured with the following precision:

	Range	Precision
Pressure	0 - 3000 psi	$\pm$ 2 psi
	3000 - 7500 psi	$\pm$ 5 psi
Volume	30 - 600 cc	$\pm$ 0.10 cc
Temperature	275 - 345°K	$\pm$ 0.2°K

The moles of gas used were determined with the compressibility factors from the literature. This compressibility factor was estimated to be within 0.3 percent. The reliability was based both on the accuracy of representation of the curves used for interpolation and the reliability of the literature data. The other variables were within the limits stated above. Thus the amount of each gas introduced could be determined within 0.7 percent. Since two measurements of gas were required for a binary gas mixture, the total number of moles used was within 1.4 percent.

The compressibility factor value, using the above error estimates was therefore known within 1.9 percent at the lowest pressure measurement. Above 3,000 pounds per square inch, the error in volume becomes more significant, thus the uncertainty may be as high as 2.5 percent.

TABLE 1

COMPRESSIBILITY FACTORS FOR THE BINARY SYSTEM

ETHANE - HYDROGEN SULFIDE

COMPOSITION - 0.157 Mole Fraction Ethane

	Pressure (psia.)	pP_R	Z
pT_R -- 0.770	217.0	0.181	0.379
T -- 40°F	226.6	0.189	0.304
	237.1	0.198	0.223
	251.7	0.210	0.136
	309.6	0.258	0.045
	571.6	0.477	0.081
	1563.6	1.304	0.216
	2619.6	2.186	0.353
	3759.0	3.136	0.501
	4965.0	4.143	0.652
pT_R -- 0.858	325.2	0.271	0.875
T -- 100°F	388.6	0.324	0.810
	441.2	0.368	0.760
	467.8	0.390	0.638
	482.3	0.402	0.485
	504.9	0.421	0.325
	519.7	0.434	0.241
	538.1	0.449	0.153
	615.8	0.514	0.086
	1143.8	0.954	0.156
	1805.8	1.507	0.238
	2584.8	2.157	0.334
	3465.8	2.892	0.437
	4436.8	3.702	0.549
	5490.8	4.581	0.665

COMPOSITION - 0.157 Mole Fraction Ethane

	Pressure (psia.)	PPR	Z
P^T_R -- 0.950 T -- 160°F	572.0	0.477	0.792
	695.6	0.580	0.737
	771.4	0.644	0.691
	852.2	0.711	0.625
	915.0	0.763	0.521
	944.8	0.788	0.383
	981.4	0.819	0.238
	1462.0	1.220	0.220
	2492.0	2.079	0.342
	3618.0	3.019	0.471
	4344.0	3.624	0.552
	5156.0	4.302	0.641

COMPOSITION - 0.242 Mole Fraction Ethane

	Pressure (psia.)	PPR	Z
P^T_R -- 0.778 T -- 40°F	263.8	0.230	0.317
	282.3	0.246	0.252
	286.9	0.250	0.167
	300.2	0.261	0.082
	389.8	0.339	0.062
	781.8	0.680	0.121
	1560.8	1.358	0.236
	2398.8	2.087	0.357
	3414.8	2.972	0.501
	4455.8	3.877	0.645
	5579.8	4.856	0.799

COMPOSITION - 0.242 Mole Fraction Ethane

	Pressure (psia.)	P_{PR}	Z
P_{TR} -- 0.872	461.6	0.402	0.749
T -- 100°F	506.2	0.440	0.680
	516.8	0.450	0.551
	548.3	0.477	0.431
	574.9	0.500	0.292
	604.2	0.526	0.138
	631.8	0.550	0.100
	941.8	0.820	0.145
	1317.8	1.147	0.198
	1790.8	1.558	0.263
	2360.8	2.054	0.340
	2991.8	2.603	0.422
	3717.8	3.235	0.515
	4531.8	3.944	0.616
	5400.8	4.700	0.722
P_{TR} -- 0.965	743.8	0.647	0.647
T -- 160°F	887.3	0.772	0.772
	1024.9	0.892	0.892
	1131.2	0.984	0.984
	1386.0	1.206	1.206
	1762.0	1.533	1.533
	2186.0	1.902	1.902
	2486.0	2.163	2.163
	2826.2	2.459	2.459
	3226.0	2.807	2.807
	3708.0	3.227	3.227
	4266.0	3.712	3.712
	4872.0	4.240	4.240
	5556.0	4.817	4.817

COMPOSITION - 0.299 Mole Fraction Ethane

	Pressure (psia.)	p_{P_R}	Z
p_{T_R} -- 0.787 T -- 40°F	290.5	0.260	0.292
	305.1	0.273	0.214
	322.7	0.289	0.128
	528.8	0.474	0.089
	970.8	0.870	0.160
	1700.8	1.523	0.275
	2483.8	2.225	0.396
	3385.8	3.033	0.531
	4319.8	3.869	0.668
	5265.8	4.717	0.803
p_{T_R} -- 0.881 T -- 100°F	401.2	0.359	0.797
	447.8	0.401	0.767
	505.4	0.453	0.727
	548.9	0.492	0.639
	571.5	0.512	0.508
	598.1	0.536	0.368
	627.7	0.562	0.215
	680.1	0.609	0.139
	974.8	0.873	0.164
	1254.8	1.124	0.207
	1641.8	1.471	0.265
	2073.8	1.858	0.327
	2565.8	2.298	0.396
	3164.8	2.835	0.479
	3860.8	3.458	0.574
	4592.8	4.114	0.671
	5367.8	4.808	0.777

COMPOSITION - 0.299 Mole Fraction Ethane

	Pressure (psia.)	pP$_R$	Z
p$_{TR}$ -- 0.976	707.8	0.634	0.736
T -- 160°F	837.5	0.750	0.662
	997.1	0.893	0.541
	1134.6	1.016	0.333
	1482.1	1.328	0.269
	2051.0	1.837	0.333
	2252.0	2.017	0.357
	2476.0	2.218	0.383
	2746.0	2.460	0.416
	3096.0	2.773	0.458
	3486.0	3.123	0.505
	3941.0	3.530	0.559
	4456.0	3.991	0.619
	5023.0	4.499	0.683

COMPOSITION - 0.409 Mole Fraction Ethane

	Pressure (psia.)	pP$_R$	Z
p$_{TR}$ -- 0.804	312.0	0.296	0.330
T -- 40°F	320.5	0.305	0.262
	329.1	0.313	0.189
	335.7	0.319	0.112
	419.0	0.398	0.074
	824.0	0.783	0.142
	1302.0	1.237	0.220
	1856.0	1.764	0.309
	2488.0	2.364	0.408
	3196.0	3.037	0.516
	3966.0	3.769	0.632
	4766.0	4.529	0.749
	5646.0	5.365	0.877

COMPOSITION - 0.409 Mole Fraction Ethane

	Pressure (psia.)	PPR	Z
PTR -- 0.900 T -- 100°F	615.0	0.584	0.577
	640.6	0.609	0.462
	665.0	0.632	0.335
	687.0	0.653	0.197
	713.8	0.678	0.135
	875.8	0.832	0.159
	1002.8	0.953	0.179
	1155.8	1.098	0.202
	1352.8	1.286	0.232
	1590.8	1.512	0.268
	1860.8	1.768	0.308
	2194.8	2.086	0.357
	2584.8	2.456	0.413
	3015.8	2.866	0.474
	3505.8	3.332	0.542
	4031.0	3.830	0.613
	4608.0	4.379	0.690
	5246.0	4.985	0.774
PTR -- 0.997 T -- 160°F	803.0	0.763	0.677
	933.6	0.887	0.603
	1080.0	1.026	0.485
	1267.6	1.205	0.318
	1525.4	1.450	0.308
	1876.2	1.783	0.344
	2181.0	2.073	0.379
	2486.0	2.362	0.417
	2881.0	2.738	0.466
	3126.0	2.971	0.497
	3400.8	3.232	0.532
	3719.8	3.535	0.571
	4075.8	3.873	0.615
	5340.8	5.075	0.766

COMPOSITION - 0.618 Mole Fraction Ethane

	Pressure (psia.)	p_R	Z
p^T_R -- 0.838 T -- 40°F	365.0 367.6 372.2 412.1 464.1	0.392 0.395 0.400 0.443 0.499	0.198 0.144 0.087 0.082 0.091
	750.1 957.1 1196.1 1750.0 2430.0	0.806 1.028 1.285 1.880 2.610	0.145 0.183 0.226 0.323 0.438
	3240.0 3706.0 4194.0 4727.0 5232.0	3.480 3.981 4.505 5.078 5.620	0.571 0.646 0.723 0.807 0.883
p^T_R -- 0.939 T -- 100°F	622.7 667.4 711.9 741.4 752.0	0.669 0.717 0.765 0.796 0.808	0.651 0.604 0.545 0.463 0.364
	762.6 852.2 875.2 929.2 1035.2	0.819 0.915 0.940 0.998 1.112	0.262 0.191 0.194 0.202 0.218
	1200.2 1435.2 1739.2 2170.1 2747.1	1.289 1.542 1.868 2.331 2.951	0.245 0.282 0.330 0.398 0.487
	3237.1 3797.0 4477.0 5274.0	3.477 4.079 4.809 5.665	0.561 0.643 0.741 0.854

COMPOSITION - 0.618 Mole Fraction Ethane

	Pressure (psia.)	pPR	Z
PTR -- 1.039 T -- 160°F	762.3	0.819	0.719
	833.8	0.896	0.680
	924.4	0.993	0.636
	1026.0	1.102	0.575
	1143.6	1.228	0.494
	1327.2	1.426	0.405
	1539.0	1.653	0.382
	1836.8	1.973	0.398
	2076.8	2.231	0.425
	2432.8	2.613	0.467
	3034.7	3.260	0.546
	3448.0	3.703	0.600
	3968.0	4.263	0.668
	4647.0	4.991	0.757
	5477.0	5.883	0.863

COMPOSITION - 0.773 Mole Fraction Ethane

	Pressure (psia.)	pPR	Z
PTR -- 0.866 T -- 40°F	369.7	0.440	0.625
	370.2	0.440	0.551
	370.8	0.441	0.477
	375.4	0.446	0.407
	376.9	0.448	0.332
	378.5	0.450	0.257
	379.8	0.452	0.182
	381.7	0.454	0.105
	386.5	0.460	0.087
	616.5	0.733	0.133
	810.4	0.964	0.172
	1001.4	1.191	0.210
	1229.4	1.462	0.254
	1507.4	1.793	0.307
	2162.4	2.572	0.429
	2974.4	3.537	0.575
	3926.4	4.670	0.740
	5105.4	6.072	0.939

COMPOSITION - 0.773 Mole Fraction Ethane

	Pressure (psia.)	P_{PR}	Z
P^T_R -- 0.970 T -- 100°F	618.6	0.736	0.651
	680.2	0.809	0.593
	739.7	0.880	0.511
	779.3	0.927	0.396
	794.9	0.945	0.259
	814.8	0.969	0.236
	839.8	0.999	0.228
	902.8	1.074	0.229
	1039.7	1.237	0.245
	1161.7	1.382	0.264
	1632.7	1.942	0.342
	2026.7	2.410	0.408
	2578.7	3.067	0.498
	3329.7	3.960	0.617
	4357.7	5.183	0.776
	5216.7	6.204	0.905
P^T_R -- 1.074 T -- 160°F	920.9	1.095	0.645
	1060.5	1.261	0.568
	1180.2	1.404	0.506
	1269.1	1.509	0.471
	1476.9	1.756	0.427
	1926.7	2.291	0.447
	2464.6	2.931	0.510
	2746.5	3.266	0.549
	3638.5	4.327	0.673
	4286.5	5.098	0.762
	5136.5	6.109	0.878

TABLE 2

COMPARISON OF CALCULATED COMPRESSIBILITY FACTORS WITH

EXPERIMENTAL VALUES *

Systems: Ethane - Hydrogen Sulfide and Methane - Hydrogen Sulfide

COMPOSITION - 0.843 Mole Fraction Hydrogen Sulfide

	C_2H_6-H_2S			C_1H_4-H_2S	
pP_R	Z	Z'		Z	Z'
		pT_R -- 0.858			
0.514	0.086	0.084			
0.954	0.156	0.149		0.193	0.150
1.507	0.238	0.231		0.233	0.233
2.157	0.334	0.323		0.333	0.325
2.892	0.437	0.425		0.437	0.427
3.702	0.549	0.532		0.546	0.535
4.581	0.665	0.650		0.663	0.654
		pT_R -- 0.950			
0.477	0.792	0.764			
0.580	0.737	0.697			
1.220	0.220	0.198		0.260	0.199
2.079	0.342	0.318		0.325	0.320
3.019	0.471	0.443		0.454	0.445
3.624	0.552	0.523		0.533	0.536
4.302	0.641	0.603		0.617	0.616

* Experimental values calculated by Pitzer's correlation
   (denoted by Z')

NOTE: The experimental compressibility factors for the two

   systems have been chosen at the same pseudo-reduced

   conditions and for similar concentrations of hydrogen

   sulfide.

COMPOSITION - 0.758 Mole Fraction Hydrogen Sulfide.

	C_2H_6-H_2S		C_1H_4-H_2S	
p_{P_R}	Z	Z'	Z	Z'

p_{T_R} -- 0.872

0.550	0.100	0.089		
0.820	0.145	0.129		
1.147	0.198	0.179		
1.558	0.263	0.239	0.265	0.242
2.054	0.340	0.309	0.323	0.312
2.603	0.422	0.386	0.399	0.390
3.235	0.515	0.471	0.467	0.475
3.944	0.616	0.565	0.581	0.569
4.700	0.722		0.682	

p_{T_R} -- 0.965

1.206	0.236	0.201		
1.533	0.279	0.244	0.286	0.247
1.902	0.330	0.294	0.320	0.297
2.163	0.366	0.329	0.349	0.332
2.456	0.407	0.369	0.388	0.373
2.807	0.454	0.415	0.434	0.419
3.227	0.511	0.469	0.486	0.473
3.712	0.576	0.529	0.546	0.533
4.240	0.644		0.611	
4.817	0.717		0.682	

COMPOSITION - 0.701 Mole Fraction Hydrogen Sulfide.

p_{T_R} -- 0.881

0.609	0.139	0.098		
0.873	0.164	0.138		
1.124	0.207	0.175		
1.471	0.265	0.227		
1.858	0.327	0.283	0.305	0.285
2.298	0.396	0.342	0.361	0.347
2.835	0.479	0.417	0.432	0.422
3.458	0.574	0.495	0.518	0.501
4.114	0.671	0.586	0.603	0.592
4.808	0.777	0.673	0.696	0.679

COMPOSITION - 0.701 Mole Fraction Hydrogen Sulfide.

	$C_2H_6-H_2S$		$C_1H_4-H_2S$	
pP_R	Z	Z'	Z	Z'

pT_R -- 0.976

1.016	0.333	0.181		
1.328	0.269	0.221		
1.837	0.333	0.288	0.322	0.292
2.017	0.357	0.332	0.335	0.335
2.218	0.383	0.339	0.361	0.143
2.460	0.416	0.383	0.393	0.387
2.773	0.458	0.412	0.436	0.416
3.123	0.505	0.457	0.477	0.461
3.530	0.559	0.507	0.525	0.511
3.991	0.619	0.564	0.582	0.568
4.499	0.683		0.646	

COMPOSITION - 0.591 Mole Fraction Hydrogen Sulfide.

pT_R -- 0.804

1.237	0.220	0.192
1.764	0.309	0.270
2.364	0.408	0.356
3.037	0.516	0.449
3.769	0.632	0.548
4.529	0.749	0.654

COMPOSITION - 0.591 Mole Fraction Hydrogen Sulfide.

P_R^P	C$_2$H$_6$-H$_2$S		C$_1$H$_4$-H$_2$S	
	Z	Z'	Z	Z'

P_R^T -- 0.900

P_R^P	Z	Z'	Z	Z'
0.653	0.197	0.108		
0.678	0.135	0.108		
0.832	0.159	0.133		
0.953	0.179	0.151		
1.098	0.202	0.172	0.424	0.177
1.286	0.232	0.200	0.325	0.203
1.512	0.268	0.232	0.292	0.237
1.768	0.308	0.268	0.302	0.273
2.086	0.357	0.313	0.334	0.319
2.456	0.413	0.366	0.383	0.372
2.866	0.474	0.422	0.442	0.428
3.332	0.542	0.483	0.509	0.490
3.830	0.613	0.548	0.573	0.556
4.379	0.690	0.617	0.644	0.625
4.985	0.774	0.692	0.724	0.701

P_R^T -- 0.997

P_R^P	Z	Z'	Z	Z'
1.026			0.572	
1.205	0.228	0.092	0.462	0.222
1.450	0.256	0.103	0.366	0.249
1.783	0.294	0.116	0.345	0.284
2.073	0.334	0.127	0.372	0.326
2.362	0.373	0.131	0.398	0.365
2.738	0.423	0.141	0.444	0.414
2.971	0.454	0.149	0.474	0.444
3.232	0.487	0.157	0.512	0.477
3.535	0.525	0.162	0.542	0.515
3.873	0.568	0.169	0.584	0.557
5.075	0.712	0.203	0.724	0.699

COMPOSITION - 0.382 Mole Fraction Hydrogen Sulfide.

	$C_2H_6-H_2S$			$C_1H_4-H_2S$	
P_{PR}	Z	Z'		Z	Z'
		P_{TR} -- 0.838			
0.400	0.087	0.064			
0.443	0.082	0.070			
0.499	0.091	0.080			
0.806	0.145	0.129			
1.028	0.183	0.160			
1.285	0.226	0.196			
1.880	0.323	0.285			
2.610	0.438	0.387			
3.480	0.571	0.507			
3.981	0.646	0.575			
4.505	0.723	0.642			
5.078	0.807	0.710			
		P_{TR} -- 0.939			
0.808	0.364	0.133			
0.819	0.262	0.135			
0.915	0.191	0.151			
0.940	0.194	0.154			
0.998	0.202	0.163			
1.112	0.218	0.180			
1.289	0.245	0.206			
1.542	0.282	0.242			
1.868	0.330	0.288			
2.331	0.398	0.353			
2.951	0.487	0.436			
3.477	0.561	0.501			
4.079	0.643	0.578			
4.809	0.741	0.666			
5.665	0.854	0.773			

COMPOSITION - 0.382 Mole Fraction Hydrogen Sulfide.

	C_2H_6-H_2S		C_1H_4-H_2S	
p_{PR}	Z	Z'	Z	Z'

p_{TR} -- 1.039

1.653	0.382	0.302		
1.973	0.398	0.333		
2.231	0.425	0.362	0.433	0.367
2.613	0.467	0.404	0.463	0.410
3.260	0.546	0.480	0.532	0.487
3.703	0.600	0.531	0.583	0.539
4.263	0.668	0.599	0.644	0.607
4.991	0.757	0.680	0.724	0.690

COMPOSITION - 0.227 Mole Fraction Hydrogen Sulfide.

p_{TR} -- 0.866

0.460	0.087	0.075
0.733	0.133	0.117
0.964	0.172	0.151
1.191	0.210	0.184
1.462	0.254	0.226
1.793	0.307	0.272
2.572	0.429	0.382
3.537	0.575	0.512
4.670	0.740	0.658

p_{TR} -- 0.970

0.999	0.228	0.179
1.074	0.229	0.188
1.237	0.245	0.210
1.382	0.264	0.229
1.942	0.342	0.302
2.410	0.408	0.385
3.067	0.498	0.454
3.960	0.617	0.556